

**From:** [Rhonda Banks Thompson](#)  
**To:** [Gudrun Thompson](#);  
**cc:** [Elizabeth Basil](#); [Sara Bazemore](#); [Thom W. Berry](#); [Clair Boatwright](#);  
[Joseph Eller](#); [Jody Hamm](#); [Adam Myrick](#); [Nancy C. Whittle](#);  
[jhudson@santecooper.com](mailto:jhudson@santecooper.com);  
**Subject:** Re: extension request--Pee Dee Draft NOMA  
**Date:** Wednesday, October 29, 2008 5:26:56 PM

---

Dear Ms. Thompson,

The Bureau of Air Quality (BAQ) has agreed to accept comments from the Southern Environmental Law Center (SELC) on the Draft Notice of MACT Approval (NOMA) for the proposed Pee Dee Generating Station until November 20, 2008. This agreement is between the BAQ and SELC and does not extend the public comment period that ends November 6, 2008.

Please note that the BAQ became aware of your FOI request on October 15, 2008, and we have worked diligently to pull all requested information together in a timely manner. All requested information was delivered to our FOI office today and should be available for your review.

We apologize for any inconvenience this matter may have caused. If you have further questions or concerns, please contact me at (803)898-4391 or [thompsrb@dhec.sc.gov](mailto:thompsrb@dhec.sc.gov)

Sincerely,

Rhonda B. Thompson, P.E.  
Assistant Bureau Chief  
Bureau of Air Quality - SCDHEC  
2600 Bull Street  
Columbia, SC 29201  
(803)898-4391 (phone)  
(803)898-4117 (fax)  
New E-mail Address: "thompsrb@dhec.sc.gov"

>>> Gudrun Thompson <[gthompson@selcnc.org](mailto:gthompson@selcnc.org)> 10/29/2008 10:52 AM  
>>>  
October 29, 2008

Dear Ms. Thompson,

As you know, the Southern Environmental Law Center (SELC) is planning to submit comments on the Draft Notice of MACT Availability (Draft NOMA) for the proposed Pee Dee Generating Station. Due to the difficulty I have experienced obtaining access to certain public records in the possession of the Bureau of Air Quality (BAQ) that are central to our review of the Draft NOMA, I write to request an extension of the deadline to file written comments on the Draft NOMA.

The Draft NOMA for was noticed for public comment on September 23, 2008. On September 25, 2008, I submitted a request to the DHEC Freedom of Information Center (FOI Center) under the South Carolina Freedom of Information Act, S.C. Code 30-4-10 et seq., requesting documents related to the Draft NOMA. I have since contacted the FOI Center multiple times, but have been told that the documents were not available. It is my understanding that the documents were to have been made available on Monday, October 27, 2008 (already past the statutory deadline). The documents still have not been made available and I was informed yesterday that BAQs attorney is still in the process of reviewing them. As a result of DHECs failure to provide these documents in a timely manner, we have been deprived of the opportunity to prepare meaningful comments on the Draft NOMA by the November 6, 2008 comment deadline. Our consultant advises me that he will require at least two weeks to prepare his technical analysis once he has received the requested documents. Therefore, I respectfully request that SELC be allowed until November 20, 2008 to file comments, and that our comments submitted on that date be considered timely filed into the administrative record of this permitting decision.

Thank you for your consideration of this request. I appreciate your prompt attention to this matter. Please contact me at (919) 967-1450 or via email at [gthompson@selcnc.org](mailto:gthompson@selcnc.org) if you have any questions, and please respond in writing with your response to this request.

Sincerely,

Gudrun Elise Thompson  
Staff Attorney  
Southern Environmental Law Center  
200 West Franklin St., Suite 330  
Chapel Hill, NC 27516  
(919) 967-1450  
[gthompson@selcnc.org](mailto:gthompson@selcnc.org)

PRIVILEGE AND CONFIDENTIALITY NOTICE

This message is intended only for the addressee(s) and may contain information that is privileged, confidential and/or otherwise exempt from disclosure under applicable law. If you are not the intended recipient, you are hereby notified that any dissemination, distribution, or copying of this communication or other use of a transmission received in error is strictly prohibited. If you have received this transmission in error, please notify me immediately at the above telephone number.

[Charleston Business Journal](#) > [November 26, 2007](#) > [News](#)

## A burning issue

By Molly Parker  
Staff Writer

“Sixteen, please.” Giving an order laced with a Southern drawl, Bill McCall Jr. directed the elevator operator seated atop a five-gallon bucket to take him to the top of the boiler tower, a critical piece of the fourth power unit under construction at Santee Cooper’s coal-fired facility in rural Cross.

Donning hard hats and safety goggles, McCall, who is Santee Cooper’s chief operating officer, and two of his senior-level colleagues stepped out onto the open-planked structure. From this vantage point, some 238 feet up in the air, heaps of coal below look like dark rolling hills.

Train cars bring in 10,000 tons a day of coal that is crushed as fine as baby powder and blown into a boiler that creates a hot steam—reaching temperatures as high as 1,055 degrees Fahrenheit—which spins a turbine that converts energy from a mechanical to an electrical state. It is then transmitted down three conductors to a transformer, jumped to 230,000 volts and shipped to the power grid.

It’s the means by which electricity is provided to thousands of South Carolina businesses and homes, yet all the while, these towering structures spew noxious pollutants into the air—chief among them mercury, carbon dioxide, particulate matter and sulfur dioxide—though far less than they once did.

It is these chemical emissions—an inevitable byproduct of coal-generated power—that have become central in a debate about whether Santee Cooper should build another coal plant 70 miles northeast near Kingsburg on 2,700 acres of wetlands and pine forest neighboring the Great Pee Dee River.

 [E-Mail This Article](#)  
 [Printer-Friendly Version](#)



photo/Andy Owens

Cooling towers emit steam at Santee Cooper’s Cross Generating Station along the shores of Lake Moultrie. Santee Cooper has plans to build a similar station on the banks of the Great Pee Dee River in Florence County.







The state-owned utility expects to face a 525-megawatt shortfall in just five years without it, which Santee Cooper says will hamper the state's ability to attract business and industry. Santee Cooper promises that its facility, when built, will be the cleanest coal plant in the nation, perhaps in the world. That notion has been challenged by environmental groups hoping to thwart plans by convincing the state Department of Health and Environmental Control that it should not issue a permit for the plant.

"The fact that they say it doesn't make it so," said Blan Holman, an attorney for the Southern Environmental Law Center, which has threatened legal action as an alternative. Environmental evolution

Some 60% of the footprint of each coal unit is made up of environmental controls. High-pressure fans suck the exhaust gas through a selective catalytic reduction process that strips it of nitrogen oxide, where it is run through a precipitator that removes particulate matter to the scrubbers.

Standing atop the Cross plant on a recent day, McCall pointed to the four massive scrubbers, one for each plant, outfitted with octopus-like metal tentacles that remove sulfur dioxide by shooting a mixture of limestone and water known as slurry at the exhaust gas waste, produced from of the combustion process.

When the first scrubber was built of steel and rubber nearly 25 years ago, it removed only 70% of sulfur dioxide, compared to the newest one made of concrete and tile that cleans away 96% of the pollutants shown to increase respiratory illnesses when present in the air.

The first Cross unit went online in 1983, the third at the beginning of this year. The fourth unit, upon which McCall stood, is still under construction.

Over the past two decades, the environmental controls have tightened and improved for coal-fired facilities, requiring less space in return for more efficiency.

The four units combined that will be running by 2009 are permitted to emit the same amount

of pollution as the two older units were allowed to cough out for a decade.

“This is what you call evolution,” he said.

All the units have now been updated to remove at least 93% of sulfur dioxide before the gas heads out the smoke stack and into the environment. The new coal units near the Pee Dee River would do even better, he said, removing 97% of sulfur dioxide, McCall said.

This evolution includes turning once-buried waste into usable products. For instance, oxygen is pumped into the scrubber to create calcium sulfate, also known as synthetic gypsum.

American Gypsum, a new \$125 million, 100-employee plant in Georgetown, is expected to begin operating by year’s end. The plant will take calcium sulfate generated at Santee Cooper’s Cross and Winyah generating stations and turn it into wall board.

“I feel like we’ve been a research and development lab for this industry,” he said.

### **Economic consequences**

Across the state, the economy would suffer, McCall said, if Santee Cooper could not deliver safe and reliable power, as it is mandated to do by state law.

But the environmental activists have painted their opposition with an economic brush as well.

The problem, said Holman, is that the new plant would eat into the region’s “increment,” or the clean-air budget for the area as measured by pollutants.

That budget is meant to prevent an area from moving into the so-called “nonattainment” status under the Clean Air Act that would threaten federal transportation dollars and future permitting applications for businesses.

“We’re dealing with a limited shared resource, which means we need to think carefully about how to dole it out,” he said. “Which would the region rather have, a tax-exempt coal plant staffed by 100 people, or several tax-paying Vought facilities employing thousands?”

Of particular concern is the plant’s proximity

to Cape Romain, a refuge owned by the U.S. Fish and Wildlife Service, which in 1997 identified that spot along with seven other national refuges as having the “highest air pollution threat.”

The air quality standards are stricter for the refuge, as with other congressionally designated areas, said Gudrun Thompson, also an attorney with the law center.

### **Environmental**

Santee Cooper spokeswoman Laura Varn challenged the claim that the utility’s presence in Florence County will thwart other businesses. The plant will emit less pollutants than the permit would allow, she said, pointing to results from the new mercury monitoring system the utility installed a year ago to accurately test the tonnage it spits out.

Preliminary results found that the two units tested emit roughly 30 to 40 pounds per year, which would equate to about 160 pounds for all four units, well under the 187.2 pounds the plant is permitted to emit in total.

Critics argue even trace amounts of mercury can do significant damage because it can seep into the water and contaminate the fish population. DHEC already recommends eating no more than one serving per month of fish caught in certain areas where high levels of mercury have been detected.

Holman’s organization and the neighbors closest to the plant would like Santee Cooper to turn away from coal altogether.

“There’s no such thing as clean coal,” he said. “That’s like a healthy cigarette.”

They contend that Santee Cooper has yet to look at a comprehensive conservation package such as the one Charlotte-based Duke Energy has filed with the Public Service Commission of South Carolina.

Duke, which is also awaiting approval in North Carolina and Indiana, claims it can retire nearly 800 megawatts of energy that coal plants would otherwise produce by passing on the costs for efficiency upgrades to customers in the same way new plant construction can be passed on through rate increases.

McCall said it's easy to point fingers when you are not the one legally charged with keeping the lights on.

"I hope you know we don't want to build one," he said once back on the ground. "We build a plant only because we need it. I think some people believe we are out here trying to build a plant and we don't want to build a plant. This is a lot of work."

*Molly Parker is a staff writer for the Business Journal. E-mail her directly at [mparker@setcommmedia.com](mailto:mparker@setcommmedia.com).*

[SUBSCRIBE](#) | [REPRINTS](#) | [CONTACT US](#)

© 2007 Copyright [Setcom Media, Inc.](#), All Rights Reserved.  
Phone: 843-849-3100 Fax: 843-849-3122



33. Why was the timetable accelerated?

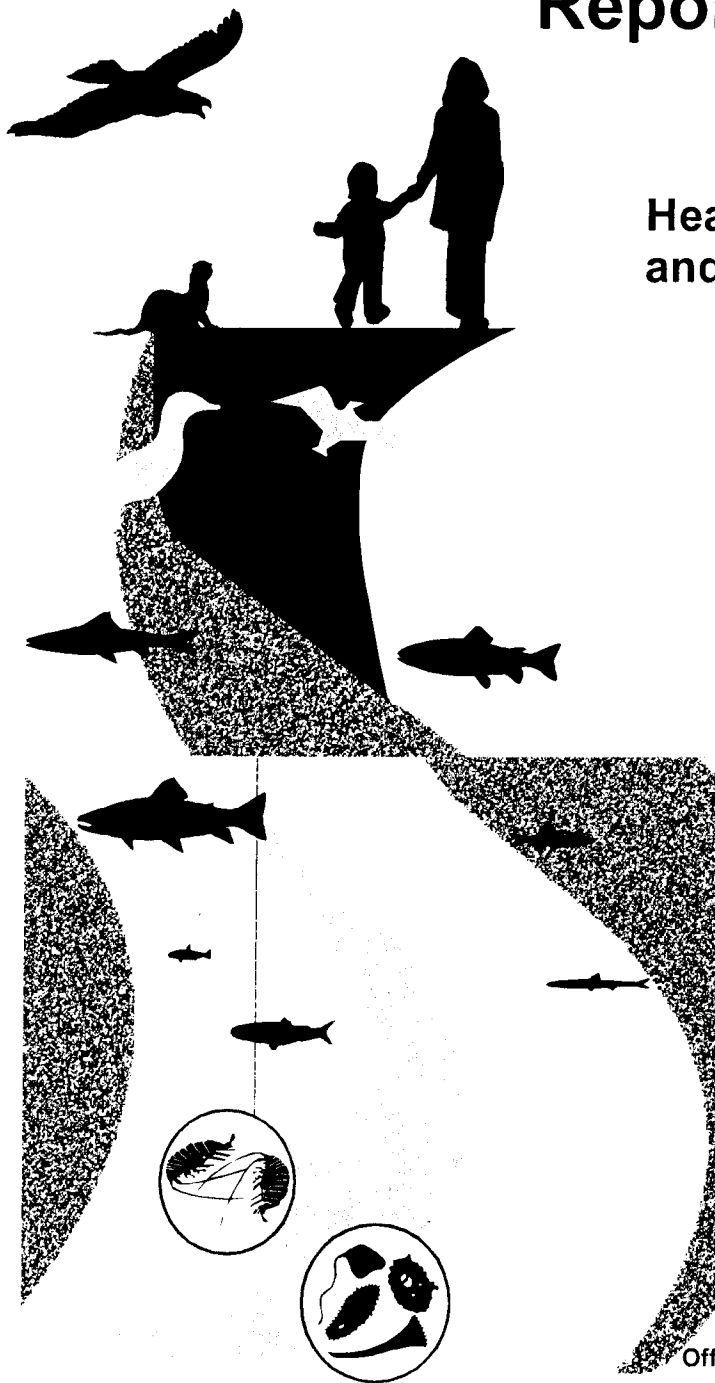
**When the generation planning process was completed in early 2006, the optimal plan called for a coal-fired generating unit to be operational as soon as possible, but no later than 2014. The March, 2006 Board Resolution authorized management to take actions it deemed necessary or appropriate to construct a 600 MW coal unit to begin operation as soon as possible but not later than 2014. After further analysis and additional information, it was determined that the unit could be built as early as 2012 at an additional construction cost of less than 1.5%. Advancing the project schedule is expected, among other things, to save on fuel and purchased power costs, eliminate construction of a gas turbine in 2011, minimize the cost of any generating fleet outage, and allow the use of duplicate designs for some equipment thereby saving on spare parts inventory, all of which are expected to offset the additional construction cost. In May, 2006, the Santee Cooper Board approved an expedited date of 2012 and revised budget.**

34. What accounts for the public announcements stating "Plans call for the 600-megawatt (MW) pulverized coal facility near Kingsburg, SC to begin commercial operation in January 2014" as recently as April 21, 2006 – yet the permit includes 2 ea. 660 MW facilities? Explain what the plans are for a second facility?

**A second unit at the Pee Dee site was originally contemplated in 1983. The 2005/2006 generation planning process recommended one 600 MW coal unit to be built as soon as possible, but no later than 2014. Following the construction and operation of the Pee Dee unit, nuclear generation is recommended. However, Santee Cooper recognizes that there are inherent risks in the timely construction of a nuclear facility given the length of time since construction of a nuclear facility within the United States. Given the fact that the need for electricity will continue to grow, even despite conservation and efficiency measures, it is prudent for Santee Cooper to be prepared to build alternatives should the re-emergence of nuclear construction within the United States be delayed.**

# Mercury Study Report to Congress

## Volume V: Health Effects of Mercury and Mercury Compounds



Office of Air Quality Planning & Standards  
and  
Office of Research and Development



**MERCURY STUDY REPORT TO CONGRESS**

**VOLUME V:**

**HEALTH EFFECTS OF MERCURY AND MERCURY COMPOUNDS**

**December 1997**

**Office of Air Quality Planning and Standards  
and  
Office of Research and Development  
U.S. Environmental Protection Agency**

# TABLE OF CONTENTS

	<u>Page</u>
U.S. EPA AUTHORS .....	iv
SCIENTIFIC PEER REVIEWERS .....	v
WORK GROUP AND U.S. EPA/ORD REVIEWERS .....	viii
LIST OF TABLES .....	ix
LIST OF FIGURES .....	xii
LIST OF SYMBOLS, UNITS AND ACRONYMS .....	xiii
EXECUTIVE SUMMARY .....	ES-1
1. INTRODUCTION .....	1-1
2. TOXICOKINETICS .....	2-1
2.1 Absorption .....	2-1
2.1.1 Elemental Mercury .....	2-1
2.1.2 Inorganic Mercury .....	2-2
2.1.3 Methylmercury .....	2-3
2.2 Distribution .....	2-4
2.2.1 Elemental Mercury .....	2-4
2.2.2 Inorganic Mercury .....	2-4
2.2.3 Methylmercury .....	2-5
2.3 Metabolism .....	2-6
2.3.1 Elemental Mercury .....	2-6
2.3.2 Inorganic Mercury .....	2-6
2.3.3 Methylmercury .....	2-6
2.4 Excretion .....	2-7
2.4.1 Elemental Mercury .....	2-7
2.4.2 Inorganic Mercury .....	2-8
2.4.3 Methylmercury .....	2-8
2.5 Biological Monitoring .....	2-9
2.5.1 Elemental Mercury .....	2-9
2.5.2 Inorganic Mercury .....	2-11
2.5.3 Methylmercury .....	2-11
2.5.4 Methods of Analysis for Measuring Mercury in Biological Samples .....	2-12
2.6 Studies on Pharmacokinetic Models .....	2-12
2.6.1 Introduction .....	2-12
2.6.2 Inorganic mercury .....	2-13
2.6.3 Methylmercury .....	2-13
2.6.4 Discussion .....	2-15
3. BIOLOGICAL EFFECTS .....	3-1
3.1 Elemental Mercury .....	3-1
3.1.1 Critical Noncancer Data .....	3-1
3.1.2 Cancer Data .....	3-5
3.1.3 Other Data .....	3-9

## TABLE OF CONTENTS (continued)

	<u>Page</u>
3.2 Inorganic Mercury .....	3-35
3.2.1 Critical Noncancer Data .....	3-35
3.2.2 Cancer Data .....	3-39
3.2.3 Other Data .....	3-43
3.3 Methylmercury .....	3-59
3.3.1 Critical Noncancer Data .....	3-59
3.3.2 Cancer Data .....	3-66
3.3.3 Other Data .....	3-73
4. SUSCEPTIBLE POPULATIONS .....	4-1
5. INTERACTIONS .....	5-1
6. HAZARD IDENTIFICATION AND DOSE-RESPONSE ASSESSMENT .....	6-1
6.1 Background .....	6-1
6.1.1 Hazard Identification .....	6-1
6.1.2 Dose-response Assessment .....	6-4
6.2 Hazard Identification for Mercury .....	6-7
6.2.1 Developmental Effects .....	6-8
6.2.2 Germ Cell Mutagenicity .....	6-11
6.2.3 Carcinogenic Effects .....	6-13
6.3 Dose-Response Assessment For Mercury .....	6-16
6.3.1 Systemic Noncancer Effects .....	6-16
6.3.2 Developmental Effects .....	6-54
6.3.3 Germ Cell Mutagenicity .....	6-55
6.3.4 Carcinogenic Effects .....	6-55
6.4 Risk Assessments Done By Other Groups .....	6-56
6.4.1 Food and Drug Administration .....	6-56
6.4.2 ATSDR .....	6-57
6.4.3 Department of Energy .....	6-57
6.4.4 National Institute of Environmental Health Sciences (NIEHS) .....	6-58
6.4.5 Department of Labor .....	6-58
6.4.6 Various States .....	6-58
6.4.7 World Health Organization .....	6-58
6.4.8 ACGIH .....	6-59
7. ONGOING RESEARCH AND RESEARCH NEEDS .....	7-1
7.1 Ongoing Research .....	7-1
7.2 Research Needs .....	7-3
8. REFERENCES .....	8-1

## TABLE OF CONTENTS (continued)

	<u>Page</u>
APPENDIX A DOSE CONVERSIONS .....	A-1
APPENDIX B SUMMARIES FOR THE INTEGRATED RISK INFORMATION SYSTEM (IRIS) .....	B-1
APPENDIX C ATTENDEES OF U.S. EPA PEER REVIEW WORKSHOP ON MERCURY ISSUES .....	C-1
APPENDIX D UNCERTAINTY ANALYSIS OF THE METHYLMERCURY RfD .....	D-1

## U.S. EPA AUTHORS

### Principal Authors:

Beth Hassett-Sipple  
Office of Air Quality  
Planning and Standards  
Research Triangle Park, NC

Rita Schoeny, Ph.D.  
Office of Water  
Washington, DC

Jeff Swartout  
National Center for Environmental  
Assessment-Cincinnati  
Office of Research and Development  
Cincinnati, OH

### Contributing Authors:

Kathryn R. Mahaffey, Ph.D.  
National Center for Environmental  
Assessment-Washington  
Office of Research and Development  
Washington, DC

Glenn E. Rice  
National Center for Environmental  
Assessment-Cincinnati  
Office of Research and Development  
Cincinnati, OH

## SCIENTIFIC PEER REVIEWERS

Dr. William J. Adams\*  
Kennecott Utah Corporation

Dr. Brian J. Allee  
Harza Northwest, Incorporated

Dr. Thomas D. Atkeson  
Florida Department of Environmental  
Protection

Dr. Donald G. Barnes\*  
U.S. EPA Science Advisory Board

Dr. Steven M. Bartell  
SENES Oak Ridge, Inc.

Dr. David Bellinger\*  
Children's Hospital, Boston

Dr. Nicolas Bloom\*  
Frontier Geosciences, Inc.

Dr. Mike Bolger  
U.S. Food and Drug Administration

Dr. Peter Botros  
U.S. Department of Energy  
Federal Energy Technology Center

Thomas D. Brown  
U.S. Department of Energy  
Federal Energy Technology Center

Dr. Dallas Burtraw\*  
Resources for the Future

Dr. Thomas Burbacher\*  
University of Washington  
Seattle

Dr. James P. Butler  
University of Chicago  
Argonne National Laboratory

Elizabeth Campbell

U.S. Department of Energy  
Policy Office, Washington D.C.

Dr. Rick Canady  
Agency for Toxic Substances and Disease  
Registry

Dr. Rufus Chaney  
U.S. Department of Agriculture

Dr. Joan Daisey\*  
Lawrence Berkeley National Laboratory

Dr. John A. Dellinger\*  
Medical College of Wisconsin

Dr. Kim N. Dietrich\*  
University of Cincinnati

Dr. Tim Eder  
Great Lakes Natural Resource Center  
National Wildlife Federation for the  
States of Michigan and Ohio

Dr. Lawrence J. Fischer\*  
Michigan State University

Dr. William F. Fitzgerald  
University of Connecticut  
Avery Point

A. Robert Flaak\*  
U.S. EPA Science Advisory Board

Dr. Bruce A. Fowler\*  
University of Maryland at Baltimore

Dr. Katherine Flegal  
National Center for Health Statistics

Dr. Steven G. Gilbert\*  
Biosupport, Inc.

Dr. Cynthia C. Gilmour\*  
The Academy of Natural Sciences



## SCIENTIFIC PEER REVIEWERS (continued)

Dr. Robert Goyer  
National Institute of Environmental Health  
Sciences

Dr. George Gray  
Harvard School of Public Health

Dr. Terry Haines  
National Biological Service

Dr. Gary Heinz\*  
Patuxent Wildlife Research Center

Joann L. Held  
New Jersey Department of Environmental  
Protection & Energy

Dr. Robert E. Hueter\*  
Mote Marine Laboratory

Dr. Harold E. B. Humphrey\*  
Michigan Department of Community Health

Dr. James P. Hurley\*  
University of Wisconsin  
Madison

Dr. Joseph L. Jacobson\*  
Wayne State University

Dr. Gerald J. Keeler  
University of Michigan  
Ann Arbor

Dr. Ronald J. Kendall\*  
Clemson University

Dr. Lynda P. Knobeloch\*  
Wisconsin Division of Health

Dr. Leonard Levin  
Electric Power Research Institute

Dr. Steven E. Lindberg\*  
Oak Ridge National Laboratory

Dr. Genevieve M. Matanoski\*  
The Johns Hopkins University

Dr. Thomas McKone\*  
University of California  
Berkeley

Dr. Malcolm Meaburn  
National Oceanic and Atmospheric  
Administration  
U.S. Department of Commerce

Dr. Michael W. Meyer\*  
Wisconsin Department of Natural Resources

Dr. Maria Morandi\*  
University of Texas Science Center at Houston

Dr. Paul Mushak  
PB Associates

Harvey Ness  
U.S. Department of Energy  
Federal Energy Technology Center

Dr. Christopher Newland\*  
Auburn University

Dr. Jerome O. Nriagu\*  
The University of Michigan  
Ann Arbor

William O'Dowd  
U.S. Department of Energy  
Federal Energy Technology Center

Dr. W. Steven Otwell\*  
University of Florida  
Gainesville

Dr. Jozef M. Pacyna  
Norwegian Institute for Air Research

Dr. Ruth Patterson  
Cancer Prevention Research Program  
Fred Gutchinson Cancer Research Center

## SCIENTIFIC PEER REVIEWERS (continued)

Dr. Donald Porcella  
Electric Power Research Institute

Dr. Deborah C. Rice\*  
Toxicology Research Center

Samuel R. Rondberg\*  
U.S. EPA Science Advisory Board

Charles Schmidt  
U.S. Department of Energy

Dr. Pamela Shubat  
Minnesota Department of Health

Dr. Ellen K. Silbergeld\*  
University of Maryland  
Baltimore

Dr. Howard A. Simonin\*  
NYSDEC Aquatic Toxicant Research Unit

Dennis Smith  
U.S. Department of Energy  
Federal Energy Technology Center

Dr. Ann Spacie\*  
Purdue University

Dr. Alan H. Stern  
New Jersey Department of Environmental  
Protection & Energy

Dr. David G. Strimaitis\*  
Earth Tech

Dr. Edward B. Swain  
Minnesota Pollution Control Agency

Dr. Valerie Thomas\*  
Princeton University

Dr. M. Anthony Verity  
University of California  
Los Angeles

\*With EPA's Science Advisory Board, Mercury Review Subcommittee

## WORK GROUP AND U.S. EPA/ORD REVIEWERS

### Core Work Group Reviewers:

Dan Axelrad, U.S. EPA  
Office of Policy, Planning and Evaluation

Angela Bandemehr, U.S. EPA  
Region 5

Jim Darr, U.S. EPA  
Office of Pollution Prevention and Toxic  
Substances

Thomas Gentile, State of New York  
Department of Environmental Conservation

Arnie Kuzmack, U.S. EPA  
Office of Water

David Layland, U.S. EPA  
Office of Solid Waste and Emergency Response

Karen Levy, U.S. EPA  
Office of Policy Analysis and Review

Steve Levy, U.S. EPA  
Office of Solid Waste and Emergency Response

Lorraine Randecker, U.S. EPA  
Office of Pollution Prevention and Toxic  
Substances

Joy Taylor, State of Michigan  
Department of Natural Resources

### U.S. EPA/ORD Reviewers:

Robert Beliles, Ph.D., D.A.B.T.  
National Center for Environmental Assessment  
Washington, DC

Eletha Brady-Roberts  
National Center for Environmental Assessment  
Cincinnati, OH

Annie M. Jarabek  
National Center for Environmental Assessment  
Research Triangle Park, NC

Matthew Lorber  
National Center for Environmental Assessment  
Washington, DC

Susan Braen Norton  
National Center for Environmental Assessment  
Washington, DC

Terry Harvey, D.V.M.  
National Center for Environmental Assessment  
Cincinnati, OH

## LIST OF TABLES

	<u>Page</u>
ES-1	Summary of U.S. EPA Hazard Identification/Dose-response Assessment for Mercury and Mercury Compounds . . . . . ES-6
2-1	Reference Values for Total Mercury Concentrations in Biological Media for the General Population . . . . . 2-10
2-2	Analytical Methods for the Detection of Mercury in Biological Samples . . . . . 2-12
3-1	Carcinogenic Effects of Elemental Mercury in Humans: Epidemiological Studies . . . . . 3-7
3-2	Lethality of Elemental Mercury in Humans: Case Studies . . . . . 3-9
3-3	Lethality of Elemental Mercury in Animals: Inhalation Exposure . . . . . 3-10
3-4	Neurotoxicity of Elemental Mercury in Humans: Case Studies . . . . . 3-11
3-5	Neurotoxicity of Elemental Mercury in Humans: Epidemiological Studies . . . . . 3-13
3-6	Neurotoxicity of Elemental Mercury in Animals: Inhalation Exposure . . . . . 3-15
3-7	Renal Toxicity of Elemental Mercury in Humans: Case Studies . . . . . 3-16
3-8	Renal Toxicity of Elemental Mercury in Humans: Epidemiological Studies . . . . . 3-17
3-9	Renal Toxicity of Elemental Mercury in Animals: Inhalation Exposure . . . . . 3-18
3-10	Respiratory Toxicity of Elemental Mercury in Humans: Case Studies . . . . . 3-18
3-11	Respiratory Toxicity of Elemental Mercury in Animals: Inhalation Exposure . . . . . 3-20
3-12	Cardiovascular Toxicity of Elemental Mercury in Humans: Case Studies . . . . . 3-21
3-13	Cardiovascular Toxicity of Elemental Mercury in Humans: Epidemiological Studies . . . . . 3-21
3-14	Cardiovascular Toxicity of Elemental Mercury in Animals: Inhalation Exposure . . . . . 3-22
3-15	Gastrointestinal Toxicity of Elemental Mercury in Humans: Case Studies . . . . . 3-23
3-16	Gastrointestinal Toxicity of Elemental Mercury in Animals: Inhalation Exposure . . . . . 3-24
3-17	Hepatic Toxicity of Elemental Mercury in Humans: Case Study . . . . . 3-24
3-18	Hepatic Toxicity of Elemental Mercury in Animals: Inhalation Exposure . . . . . 3-25
3-19	Hematological Toxicity of Elemental Mercury in Humans: Case Studies . . . . . 3-25
3-20	Hematological Toxicity of Elemental Mercury in Humans: Epidemiological Studies . . . . . 3-26
3-21	Immunotoxicity of Elemental Mercury in Humans: Case Study . . . . . 3-27
3-22	Immunotoxicity of Elemental Mercury in Humans: Epidemiological Studies . . . . . 3-27
3-23	Immunotoxicity of Elemental Mercury in Animals: Inhalation Exposure . . . . . 3-27
3-24	Dermal Toxicity of Elemental Mercury in Humans: Case Studies . . . . . 3-28
3-25	Developmental Toxicity of Elemental Mercury in Humans: Case Studies . . . . . 3-29
3-26	Developmental Toxicity of Elemental Mercury in Humans: Epidemiological Studies . . . . . 3-30
3-27	Developmental Toxicity of Elemental Mercury in Animals . . . . . 3-31
3-28	Reproductive Toxicity of Elemental Mercury in Humans: Epidemiological Studies . . . . . 3-32
3-29	Reproductive Toxicity of Elemental Mercury in Animals . . . . . 3-33
3-30	Genotoxicity of Elemental Mercury in Humans . . . . . 3-34
3-31	Incidence of Selected Lesions in Rats in the NTP (1993) 2-Year Gavage Study . . . . . 3-41
3-32	Incidence of Renal Tubule Tumors in Male Mice in the NTP (1993)

## LIST OF TABLES (continued)

	2-Year Gavage Study .....	3-42
3-33	Carcinogenic Effects of Inorganic Mercury in Animals: Oral Exposure .....	3-43
3-34	Lethality of Inorganic Mercury in Humans: Case Study .....	3-43
3-35	Lethality of Inorganic Mercury in Animals: Oral Exposure .....	3-44
3-36	Neurotoxicity of Inorganic Mercury in Humans: Case Studies .....	3-45
3-37	Neurotoxicity of Inorganic Mercury in Animals: Oral Exposure .....	3-45
3-38	Renal Toxicity of Inorganic Mercury in Humans: Case Studies .....	3-46
3-39	Renal Toxicity of Inorganic Mercury in Animals: Oral Exposure .....	3-46
3-40	Renal Toxicity of Inorganic Mercury in Animals: Inhalation Exposure .....	3-48
3-41	Cardiovascular Toxicity of Inorganic Mercury in Animals .....	3-48
3-42	Gastrointestinal Toxicity of Inorganic Mercury in Humans: Case Studies .....	3-49
3-43	Gastrointestinal Toxicity of Inorganic Mercury in Animals .....	3-50
3-44	Hepatic Toxicity of Inorganic Mercury in Animals .....	3-51
3-45	Immunotoxicity of Inorganic Mercury in Animals .....	3-52
3-46	Developmental Toxicity of Inorganic Mercury in Animals: Inhalation Exposure .....	3-52
3-47	Developmental Toxicity of Inorganic Mercury in Animals: Oral Exposure .....	3-54
3-48	Reproductive Toxicity of Inorganic Mercury in Humans: Case Study .....	3-56
3-49	Reproductive Toxicity of Inorganic Mercury in Animals .....	3-57
3-50	Genotoxicity of Inorganic Mercury in Humans .....	3-57
3-51	Genotoxicity of Inorganic Mercury in Animals .....	3-59
3-52	Carcinogenic Effects of Methylmercury in Humans: Epidemiological Studies .....	3-68
3-53	Carcinogenic Effects of Methylmercury in Animals: Oral Exposure .....	3-70
3-54	Lethality of Methylmercury in Humans: Case Study of Oral Exposure .....	3-73
3-55	Lethality of Methylmercury in Humans: Case Studies of Inhalation Exposure .....	3-74
3-56	Lethality of Methylmercury in Animals .....	3-74
3-57	Neurotoxicity of Methylmercury in Humans: Case Studies of Oral Exposure .....	3-77
3-58	Neurotoxicity of Methylmercury in Humans: Case Studies of Inhalation Exposure .....	3-78
3-59	Neurotoxicity of Methylmercury in Animals .....	3-80
3-60	Renal Toxicity of Methylmercury in Animals .....	3-82
3-61	Cardiovascular Toxicity of Methylmercury in Humans: Case Study .....	3-82
3-62	Cardiovascular Toxicity of Methylmercury in Animals .....	3-82
3-63	Gastrointestinal Toxicity of Methylmercury in Animals .....	3-84
3-64	Immunotoxicity of Methylmercury in Animals .....	3-84
3-65	Dermal Toxicity of Methylmercury in Humans: Epidemiological Study .....	3-85
3-66	Developmental Toxicity of Methylmercury in Humans: Case Studies .....	3-86
3-67	Developmental Toxicity of Methylmercury in Humans: Epidemiologic Studies .....	3-87
3-68	Developmental Toxicity of Methylmercury in Animals .....	3-88
3-69	Reproductive Toxicity of Methylmercury in Animals .....	3-94
3-70	Genotoxicity of Methylmercury in Humans: Case Study .....	3-95
3-71	Genotoxicity of Methylmercury in Humans: Epidemiology Study .....	3-95
3-72	Genotoxicity of Methylmercury in Cats .....	3-96
5-1	Interactions of Mercury with Other Compounds .....	5-3
6-1	Consensus Decisions of Peer Review Panel .....	6-18
6-2	Available Data on Hair:Blood Ratio (Total Hg) .....	6-24
6-3	Incidence of Effects in Iraqi Children by Exposure Group .....	6-26

## LIST OF TABLES (continued)

6-4	Incidence of Effects in Iraqi Adults by Exposure Group .....	6-26
6-5	Methylmercury Benchmark Dose Estimates (ppm hair) .....	6-28
6-6	Methylmercury Benchmark Dose Estimates (ppb blood) .....	6-28
6-7	Density-Based Dose Groupings .....	6-29
6-8	Uniform Dose Groupings .....	6-30
6-9	Benchmark Dosed Calculated on Data from Marsh et al. (1987) .....	6-30
6-10	Summary of Benchmark Doses (BMD) Estimated for Methylmercury .....	6-32
6-11	Results of Revised Denver Developmental Screening Test (DDST) Administered to Seychellois Children in Cross-sectional Study .....	6-33
6-12	Estimates of No Observed Adverse Effect Levels (NOAELs) and Lowest Observed Adverse Effect Levels (LOAELs) from Human Studies .....	6-34
6-13	Estimates of NOAELs and LOAELs from Animal Studies .....	6-39
6-14	NOAELs and LOAELs for Developmental Toxicity of Methylmercury in Animals ....	6-42
6-15	Studies in Non-Human Primates .....	6-46
7-1	Ongoing Research .....	7-1



## LIST OF FIGURES

	<u>Page</u>
6-1 Density of Data Points Relative to Hg Concentration in Hair for Iraqi Cohort Data .....	6-29

## LIST OF SYMBOLS, UNITS AND ACRONYMS

ATSDR	Agency for Toxic Substances and Disease Registry
BML	Biological monitoring level
bw	Body weight
CAA	Clean Air Act as amended in 1990
CHO	Chinese hamster ovary
C.I.	Confidence interval
CNS	Central nervous system
CRAVE	Carcinogen Risk Assessment Verification Endeavor
DDST	Denver Developmental Screen Test
DHHS	Department of Health and Human Services
DNA	Deoxyribonucleic acid
DWEL	Drinking water equivalent level
ECG	Electrocardiogram
EEG	Electroencephalogram
EPA	Environmental Protection Agency
FDA	Food and Drug Administration
GABA	Gamma aminobutyric acid
Gd	Gestation day
HEC	Human equivalent concentration
Hg	Mercury
Hg•U	Urinary mercury
IgG	Immunoglobulin G
IRIS	Integrated Risk Information System
LC <sub>50</sub>	Lethal concentration killing 50 percent of the animals tested (inhalation)
LD <sub>50</sub>	Lethal dose killing 50 percent of the animals tested
LOAEL	Lowest-observed-adverse-effect level
MF	Modifying factor
MMAD	Mass median aerodynamic diameter
MMC	Methylmercuric chloride
MMH	Methylmercuric hydroxide
MRL	Minimal risk level
MTD	Maximum tolerated dose
NAG	N-acetyl-b-glycosaminidase
NADH	Reduced nicotinamide adenine dinucleotide
NADPH	Reduced nicotinamide adenine dinucleotide phosphate
NOAEL	No-observed-adverse-effect level
NS	Not specified
NTP	National Toxicology Program
PMA	Phenyl mercuric acetate
ppd	Postpartum day
RfD	Reference dose (oral)
RfD <sub>DT</sub>	Reference dose for developmental toxicity
RfC	Reference concentration (inhalation)
SCE	Sister chromatid exchange
SGPT	Serum glutamic-pyruvic transaminase
SH	Sulfhydryl groups

## **LIST OF SYMBOLS, UNITS AND ACRONYMS (continued)**

SMR	Standard mortality ratio
TOLD	Test of Language Development
TWA	Time-weighted average
UF	Uncertainty factor
UF <sub>A</sub>	Uncertainty factor for interspecies extrapolation
UF <sub>H</sub>	Uncertainty factor for intraspecies extrapolation (animal to human)
UF <sub>L</sub>	Uncertainty factor for use of a LOAEL
UF <sub>S</sub>	Uncertainty factor for use of a subchronic-duration study
WHO	World Health Organization

## EXECUTIVE SUMMARY

Section 112(n)(1)(B) of the Clean Air Act (CAA), as amended in 1990, directs the U.S. Environmental Protection Agency (U.S. EPA) to submit to Congress a comprehensive study on atmospheric emissions of mercury. This document, which covers the human health effects of mercury and mercury compounds, is one volume of U.S. EPA's eight-volume Report in response to this directive.

Mercury is a naturally occurring element that is found in air, water and soil. It exists in any of three valence states:  $\text{Hg}^0$  (elemental mercury),  $\text{Hg}_2^{2+}$  (mercurous mercury), or  $\text{Hg}^{2+}$  (mercuric mercury). Most of the population of the earth have some exposure to mercury as a result of normal daily activities. The general population may be exposed to mercury through inhalation of ambient air; consumption of contaminated food, water, or soil; and/or dermal exposure to substances containing mercury. In addition, some quantity of mercury is released from dental amalgam.

The health effects literature contains many investigations of populations with potentially high exposure to mercury, including industrial workers, people living near point sources of mercury emissions, people who consume large amounts of fish, and dental professionals. There also are numerous studies of populations unintentionally exposed to high levels of mercury, such as the Minamata poisoning episode in Japan. Volume IV (An Assessment Exposure to Mercury in the United States) presents measured and predicted mercury exposure for various U.S. populations.

The purpose of this volume, Volume V, is to summarize the available health effects information for mercury and mercury compounds and to present U.S. EPA's analysis for two critical pieces of the risk assessment paradigm described by the National Academy of Sciences in 1983. Specifically, this volume contains the hazard identification and dose-response assessments for three forms of mercury: elemental mercury, mercuric chloride (inorganic mercury), and methylmercury (organic mercury). In order to characterize risk for any populations, the evaluations presented in this volume must be combined with the assessment of exposure presented in Volume IV.

Volume V is not intended to be an exhaustive survey of the voluminous health effects literature available for mercury. Rather, the purpose is to present a brief survey of the studies relevant for assessing potential human health effects and to present more detailed information on those studies which form the basis for U.S. EPA's hazard identification and dose-response assessments. The three forms of mercury which are emphasized in this volume were selected based on data indicating that these are the predominant forms of mercury to which humans are exposed. In addition, examination of the published literature indicates that most health data are on these forms. It is acknowledged that certain populations can be exposed to many types of organic mercurials, such as antiseptics and pesticides. Volume V, however, deals with methylmercury except in cases where information on another organic is presented for illustrative purposes.

### Toxicokinetics

The toxicokinetics (i.e., absorption, distribution, metabolism, and excretion) of mercury is highly dependent on the form of mercury to which a receptor has been exposed. Below is a brief summary of the toxicokinetics information for elemental mercury, mercuric chloride, and methylmercury. Chapter 2 contains a more complete summary of the toxicokinetics information available for mercury.

### Elemental Mercury

The absorption of elemental mercury vapor occurs rapidly through the lungs, but it is poorly absorbed from the gastrointestinal tract. Once absorbed, elemental mercury is readily distributed throughout the body; it crosses both placental and blood-brain barriers. Elemental mercury is oxidized to inorganic divalent mercury by the hydrogen peroxidase-catalase pathway, which is present in most tissues. The distribution of absorbed elemental mercury is limited primarily by the oxidation of elemental mercury to the mercuric ion as the mercuric ion has a limited ability to cross the placental and blood-brain barriers. Once elemental mercury crosses these barriers and is oxidized to the mercuric ion, return to the general circulation is impeded, and mercury can be retained in brain tissue. The elimination of elemental mercury occurs via urine, feces, exhaled air, sweat, and saliva. The pattern of excretion is dependent on the extent to which elemental mercury has been oxidized to mercuric mercury.

### Inorganic Mercury

Absorption of inorganic mercury through the gastrointestinal tract varies with the particular mercuric salt involved. Absorption decreases with decreasing solubility. Estimates of the percentage of inorganic mercury that is absorbed vary; as much as 20% may be absorbed. Available data indicate that absorption of mercuric chloride from the gastrointestinal tract results from an electrostatic interaction with the brush border membrane and limited passive diffusion. Increases in intestinal pH, high doses of mercuric chloride causing a corrosive action, a milk diet (e.g., neonates) and increases in pinocytotic activity in the gastrointestinal tract (e.g., neonates) have all been associated with increased absorption of inorganic mercury. Inorganic mercury has a limited capacity for penetrating the blood-brain or placental barriers. There is some evidence indicating that mercuric mercury in the body following oral exposures can be reduced to elemental mercury and excreted via exhaled air. Because of the relatively poor absorption of orally administered inorganic mercury, the majority of the ingested dose in humans is excreted through the feces.

### Methylmercury

Methylmercury is rapidly and extensively absorbed through the gastrointestinal tract. Absorption information following inhalation exposures is limited. This form of mercury is distributed throughout the body and easily penetrates the blood-brain and placental barriers in humans and animals. Methylmercury transport into tissues appears to be mediated by the formation of a methylmercury-cysteine complex. This complex is structurally similar to methionine and is transported into cells via a widely distributed neutral amino acid carrier protein. Methylmercury in the body is considered to be relatively stable and is only slowly demethylated to form mercuric mercury in rats. It is hypothesized that methylmercury metabolism may be related to a latent or silent period observed in epidemiological studies observed as a delay in the onset of specific adverse effects. Methylmercury has a relatively long biological half-life in humans; estimates range from 44 to 80 days. Excretion occurs via the feces, breast milk, and urine.

### **Biological Monitoring/Pharmacokinetic Models**

Chapter 2 provides information on biological monitoring of mercury as well as a summary of the development of pharmacokinetic models for mercury. The most common biological samples analyzed for mercury are blood, urine, and scalp hair. The methods most frequently used to determine the mercury levels in these sample types include atomic absorption spectrometry, neutron activation analysis, X-ray fluorescence, and gas chromatography.

Both simple and complex multi-compartmental models have been described in the literature. A recent report (Gearhart et al. 1995) presents an approach based upon data from human, rat, and monkey data that could be used for characterizing dose-response data both adults and neonates.

## **Biological Effects**

Chapter 3 presents summary information on the toxicity of elemental mercury, mercuric mercury and methylmercury to various organ systems. The primary targets for toxicity of mercury and mercury compounds are the nervous system, the kidney, and the developing fetus. Other systems that may be affected include the respiratory, cardiovascular, gastrointestinal, hematologic, immune, and reproductive systems. For each form of mercury and each of the endpoints addressed, information from epidemiological studies, human case studies, and animal toxicity studies is summarized in tabular form. Critical studies are discussed in the accompanying text.

### Elemental Mercury

A number of epidemiological studies have been conducted that examined cancer mortality and/or morbidity among workers occupationally exposed to elemental mercury. All of these studies, however, have limitations which compromise the interpretation of their results; these limitations include small sample sizes, probable exposure to other known lung carcinogens, failure to consider confounding factors such as smoking, and/or failure to observe correlations between estimated exposure and the cancer incidence. Only one animal study was identified that examined cancer incidence in animals exposed (by injection) to elemental mercury. While tumors were found at contact sites, the study was incompletely reported as to controls and statistics and, thus, considered inadequate for the purpose of risk assessment. Findings from genotoxicity assays are limited and do not provide supporting evidence for a carcinogenic effect of elemental mercury.

Effects on the nervous system appear to be the most sensitive toxicological endpoint observed following exposure to elemental mercury. Symptoms associated with elemental mercury-induced neurotoxicity include the following: tremors, initially affecting the hands and sometimes spreading to other parts of the body; emotional lability, often referred to as "erethism" and characterized by irritability, excessive shyness, confidence loss, and nervousness; insomnia; neuromuscular changes (e.g., weakness, muscle atrophy, muscle twitching); headaches; polyneuropathy (e.g., paresthesia, stocking-glove sensory loss, hyperactive tendon reflexes, slowed sensory and motor nerve conduction velocities); and memory loss and performance deficits in test of cognitive function. At higher concentrations, adverse renal effects and pulmonary dysfunction may also be observed.

A few studies have provided suggestive evidence for potential reproductive toxicity associated with exposure to elemental mercury. Data from two studies in rats demonstrate developmental effects of elemental mercury exposure. These were behavioral changes associated with both *in utero* and perinatal exposure.

### Inorganic Mercury

There is no evidence in humans linking exposure to mercuric chloride with carcinogenic effects. Data in animals are limited. Focal hyperplasia and squamous cell papillomas of the forestomach as well as thyroid follicular adenomas and carcinomas were observed in male rats gavaged with mercuric chloride. In the same study, evidence for an increased incidence of squamous cell forestomach papillomas in female rats and renal adenomas and carcinomas in male mice were considered equivocal.



All increased tumor incidences were observed in excess of the maximum tolerated dose (MTD). In this context, the relevance of the tumors to human health evaluation has been questioned. Results from *in vitro* and *in vivo* tests for genotoxicity have been mixed and do not provide strong supporting data for carcinogenicity.

There are some data indicating that mercuric chloride may be a germ cell mutagen. Positive results have been obtained for chromosomal aberrations in multiple systems, and evidence suggests that mercuric chloride can reach female gonadal tissue.

The most sensitive general systemic adverse effect observed following exposure to inorganic mercury is the formation of mercuric mercury-induced autoimmune glomerulonephritis. The production and deposition of IgG antibodies to the glomerular basement membrane can be considered the first step in the formation of this mercuric-mercury-induced autoimmune glomerulonephritis.

Several studies in animals have evaluated the potential for developmental toxicity to occur following exposure to various inorganic salts. While the evidence suggests that developmental effects may occur, all of the studies have significant limitations.

#### Methylmercury

Three human studies that examined the relationship between methylmercury and cancer incidence were considered extremely limited because of study design inappropriate for risk assessment or incomplete data reporting. Evidence from animal studies provides limited evidence of carcinogenicity. Male ICR and B6C3F1 mice exposed orally to methylmercuric chloride were observed to have an increased incidence of renal adenomas, adenocarcinomas, and carcinomas. Renal epithelial cell hyperplasia and tumors, however, were observed only in the presence of profound nephrotoxicity suggesting that the tumors may be a consequence of reparative changes to the damaged kidneys. Tumors were observed at a single site, in a single species and sex.

Methylmercury appears to be clastogenic but not a potent mutagen. Studies have also shown evidence that methylmercury may induce mammalian germ cell chromosome aberrations. There are a number of studies in both humans and experimental animals that show methylmercury to be a developmental toxicant. Neurotoxicity in offspring is the most commonly observed effect and the effect seen at lowest exposures.

A significant body of human studies exists for evaluating the potential systemic toxicity of methylmercury. This data base is the result of studying two large scale poisoning episodes in Japan and Iraq as well as several epidemiological studies assessing populations that consume significant quantities of fish. In addition, much research on the toxicity of methylmercury has been conducted in animals including non-human primates.

The critical target for methylmercury toxicity is the nervous system. The developing fetus may be at particular risk from methylmercury exposure. Offspring born of women exposed to methylmercury during pregnancy have exhibited a variety of developmental neurological abnormalities, including the following: delayed onset of walking, delayed onset of talking, cerebral palsy, altered muscle tone and deep tendon reflexes, and reduced neurological test scores. Maternal toxicity may or may not have been present during pregnancy for those offspring exhibiting adverse effects. For the general population, the critical effects observed following methylmercury exposure are multiple central nervous system effects including ataxia and paresthesia.

A latent or silent period has been observed in some epidemiological and animal studies indicating a delay in the onset of adverse effects. It is hypothesized this delay may be related to methylmercury metabolism.

### **Sensitive Subpopulations**

A susceptible population is a group that may experience more severe adverse effects at comparable exposure levels or adverse effects at lower exposure levels than the general population. The greater response of these sensitive subpopulations may be a result of a variety of intrinsic or extrinsic factors. For mercury, the most sensitive subpopulations may be developing organisms. Data are also available indicating that other factors may be associated with the identification of sensitive subpopulations including the following: age; gender; dietary insufficiencies of zinc, glutathione, or antioxidants; predisposition for autoimmune glomerulonephritis; and predisposition for acrodynia. More information on sensitive subpopulations is presented in Chapter 4.

### **Interactions**

There are data demonstrating that a number of substances affect the pharmacokinetics and/or toxicity of mercury compounds. Of most interest is the potential interaction of selenium and mercury. Selenium is known to bioaccumulate in fish, so exposure to methylmercury from fish consumption may be associated with exposure to increased levels of selenium. There are data indicating that selenium co-administered with methylmercury can form selenium-methylmercury complexes. The formation of these complexes may temporarily prevent methylmercury-induced tissue damage but also may delay excretion of the methylmercury. Thus, formation of selenium-methylmercury complexes may not reduce methylmercury toxicity but rather may delay onset of symptoms. More information is needed to understand the possible interaction of selenium with methylmercury.

There is potential for interaction between various forms of mercury and ethanol, thiol compounds, tellurium, potassium dichromate, zinc, atrazine, and vitamins C and E.

### **Hazard Identification/Dose-Response Assessment**

The available toxicological and epidemiological evidence was evaluated, and U.S. EPA risk assessment guidelines and methodologies were applied to hazard identification for various endpoints; namely, carcinogenicity, germ cell mutagenicity, developmental toxicity, and general systemic toxicity. Data supported quantitative assessments of systemic toxicity. For elemental mercury, an inhalation reference concentration (RfC<sup>1</sup>) was calculated; oral reference doses (RfD<sup>1</sup>) were calculated for inorganic mercury and methylmercury. Data for carcinogenicity of inorganic and methylmercury were judged to be inadequate in humans and limited from animal bioassays. The carcinogenicity data for all forms of mercury evaluated were not sufficient to support a quantitative assessment. No quantitative estimates were done for developmental toxicity. Table ES-1 summarizes the hazard identification and dose-response information for elemental mercury, inorganic mercury, and organic mercury. The bases for these decisions and the methodologies applied are presented in Chapter 6.

---

<sup>1</sup> The oral RfD and the inhalation RfC are estimates (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subpopulations) that is likely to be without an appreciable risk of deleterious health effects during a lifetime.

**Table ES-1**  
**Summary of U.S. EPA Hazard Identification/Dose-response Assessment**  
**for Mercury and Mercury Compounds**

Form of Mercury	Oral RfD (mg/kg-day)	Inhalation RfC (mg/m <sup>3</sup> )	Cancer Weight-of-evidence Rating	Cancer Slope Factor	Germ Cell Mutagenicity	Developmental Toxicity Data Base Characterization
Elemental	n/a <sup>a</sup>	0.0003 <sup>b</sup>	D, not classifiable as to human carcinogenicity	n/a	Low weight of evidence	Insufficient human evidence; sufficient animal evidence
Inorganic	0.0003 <sup>c</sup> (mercuric chloride)	Not <sup>d</sup> verifiable	C, possible human carcinogen	n/a	Moderate weight of evidence	Insufficient evidence
Organic	0.0001 <sup>e</sup> (methylmercury)	n/a	C, possible human carcinogen	n/a	High weight of evidence	Sufficient human and animal data

<sup>a</sup> Not available; data do not support development of a value at this time.

<sup>b</sup> Critical effect is neurological toxicity (hand tremor; increases in memory disturbances; slight subjective and objective evidence of autoimmune dysfunction) in adults.

<sup>c</sup> Critical effect is renal toxicity resulting from an autoimmune disease caused by the accumulation of a hapten-mercury complex in the glomerular region of the kidneys.

<sup>d</sup> Data were judged insufficient for calculation of RfC.

<sup>e</sup> Critical effect is neurological toxicity in progeny of exposed women, RfD calculated using a benchmark dose (10%).

## Ongoing Research

While much data has been collected on the potential toxicity of mercury and mercury compounds, much is still unknown. Two ongoing epidemiological studies are now providing critical information on the developmental toxicity of methylmercury. One study, being conducted in the Seychelles Islands, is evaluating dose-response relationships in a human population with dietary exposures (fish) at levels believed to be in the range of the threshold for developmental toxicity. The second study, conducted in the Faroe Islands, is assessing mercury exposure in a population that consumes a relatively large quantity of marine fish and marine mammals. Children exposed to methylmercury *in utero* and followed through 6 years of age have been assessed for mercury exposure and neurological developmental. Published data from these studies are summarized in Chapter 3. Implications of ongoing research is discussed along with uncertainties in risk assessments in Chapter 6.

## Research Needs

Specifically, information is needed to reduce the uncertainties associated with the current oral RfDs and inhalation RfCs. More work with respect to both dose and duration of exposure would also allow for potentially assessing effects above the RfD/RfC. Limited evidence suggests that methylmercury and mercuric chloride are possible human carcinogens. Data are not sufficient to classify the potential carcinogenicity of elemental mercury. Research on mode of action in induction of tumors at high mercury dose will be of particular use in defining the nature of the dose response relationship for carcinogenicity. At this time data have been judged insufficient for calculation of quantitative developmental toxicity estimates for elemental and inorganic mercury; research toward this end should be encouraged. While some pharmacokinetic models have been developed additional work to ensure the

applicability of these to risk assessment should be pursued. In particular work aimed at validation of a fetal pharmacokinetic model and research in support of toxicokinetics will be useful.

## Conclusions

The following conclusions progress from those with greater certainty to those with lesser certainty.

- The three forms of mercury discussed in this Report can present a human health hazard.
- Neurotoxicity is the most sensitive indicator of adverse effects in humans exposed to elemental mercury and methylmercury.
- Immune-mediated kidney toxicity is the most sensitive indicator of toxic effects of exposure to inorganic mercury. This judgement is largely based on results in experimental animals.
- Methylmercury is a developmental toxicant in humans.
- Methylmercury is likely to be a human germ cell mutagen. This judgement is based on data from human studies, genetic toxicology studies in animals and a consideration of the pharmacokinetics of methylmercury.
- An RfD for ingested methylmercury based on neurotoxic effects observed in Iraqi children exposed *in utero* is  $1 \times 10^{-4}$  mg/kg-day. The threshold estimate derived using a benchmark dose approach is not model dependent (polynomial vs. Weibull). The estimate is not much affected by data grouping, but is dependent on response classification and on parameters used in determination of ingestion relative to measured mercury in hair.
- An RfC for inhaled elemental mercury based on neurotoxic effects in exposed workers is  $3 \times 10^{-4}$  mg/m<sup>3</sup>.
- An RfD for ingested inorganic mercury based on immune-mediated kidney effects in Brown-Norway rats is  $3 \times 10^{-4}$  mg/kg-day.
- Elemental mercury is a developmental toxicant in experimental animals. If the mechanisms of action producing developmental toxicity in animals occur in humans, elemental mercury is very likely to produce developmental effects in exposed human populations. U.S. EPA has made no estimate of dose response for developmental effects of elemental mercury.
- Methylmercury and inorganic mercury produce tumors in experimental animals at toxic doses. If the mechanisms of action which induced tumors in the animal models could occur in humans, it is possible that tumors could be induced in exposed humans by these forms of mercury. It is likely, however, that cancer would be induced only after mercury exposures in excess of those producing other types of toxic response.

There are many uncertainties associated with this analysis, due to an incomplete understanding of the toxicity of mercury and mercury compounds. The sources of uncertainty include the following:

- The data serving as the basis for the methylmercury RfD were from a population ingesting contaminated seed grain. The nutritional status of this group may not be similar to that of U.S. populations. The exposure was for a short albeit critical period of time. It is likely that there is a range of response among individuals to methylmercury exposure. The selenium status of the exposed Iraqi population is not certain, nor is it established the extent to which selenium has an effect on mercury toxicity.
- There was no NOAEL (no-observable-adverse-effect level) for estimation of a threshold for all developmental endpoints. A benchmark was estimated using a Weibull model on grouped data. Use of an estimate other than the 95% lower limit on 10% response provides alternate estimates. Other modeling approaches using data which have not been grouped provide similar estimates. Benchmark doses, NOAELs, LOAELs, from other human studies provide support for the benchmark used in the RfD.
- Ingestion levels of methylmercury associated with measured mercury in hair were estimated based on pharmacokinetic parameters derived from evaluation of the extant literature. Use of other plausible values for these parameters results in (relatively small) changes in the exposure estimate.
- While there are data to show that the developing fetus is more susceptible to methylmercury toxicity than adults, there are not sufficient data to support calculation of a separate RfD for children (vs. adults).
- The RfD for inorganic mercury is based on data in experimental animals; there is uncertainty in extrapolation to humans. It is thought that these animals constitute a good surrogate for a sensitive human subpopulation. The data were from less than lifetime exposures; there is uncertainty in extrapolation to a lifetime RfD. There was no NOAEL in the studies; there is uncertainty in extrapolation to a NOAEL or in estimation of a threshold for effects in animals.
- The RfC for elemental mercury was based on studies in exposed workers for which there is no reported NOAEL; there is uncertainty in estimating the no effect level in these populations. There is uncertainty as to whether reproductive effects could be occurring at lower exposure levels than those which produced the observed neurotoxicity.
- There are insufficient data to determine whether elemental mercury induces carcinogenic effects in experimental animals.
- Data are not sufficient to judge if elemental and inorganic mercury are germ cell mutagens.
- U.S. EPA did not formally evaluate data on mercury for reproductive effects.

To improve the risk assessment for mercury and mercury compounds, U.S. EPA would need the following:

- Results from ongoing studies in human populations with measurable exposure to methylmercury.
- Results for immune-mediated kidney effects from lifetime studies of sensitive animals exposed to inorganic mercury. Definitive data from human studies on effects of exposure to inorganic mercury.
- Data on inhalation effects of inorganic mercury exposure.
- Dose response data for developmental effects of elemental and inorganic mercury.
- Reproductive studies and analysis for all forms of mercury.
- Data on mode of action of inorganic and methylmercury tumor induction.
- Validated physiologically-based pharmacokinetic models for mercury which include a fetal component.

Based on the extant data and knowledge of developing studies, the following outcomes can be expected:

- Human populations exposed to sufficiently high levels of elemental mercury will have increased incidence of neurotoxic effects.
- Human populations exposed to sufficiently high levels of methylmercury either *in utero* or *post partum* will have increased incidence of neurotoxic effects.
- Human populations exposed to sufficiently high levels of inorganic mercury will have increased incidence of systemic effects including immune-mediated kidney effects.
- The RfDs and RfC calculated by U.S. EPA for systemic toxic effects of mercury are expected to be amounts of exposure that can be incurred on a daily basis for a lifetime without anticipation of adverse effects. This expectation is for populations including susceptible subpopulations.
- The RfDs are protective against carcinogenic effects; tumor induction in animals was observed only at doses likely to produce systemic toxic effects.

## 1. INTRODUCTION

Section 112(n)(1)(B) of the Clean Air Act (CAA), as amended in 1990, requires the U.S. Environmental Protection Agency (U.S. EPA) to submit a study on atmospheric mercury emissions to Congress. The sources of emissions that must be studied include electric utility steam generating units, municipal waste combustion units and other sources, including area sources. Congress directed that the Mercury Study evaluate many aspects of mercury emissions, including the rate and mass of emissions, their health and environmental effects, technologies to control such emissions and the costs of such controls.

In response to this mandate, U.S. EPA has prepared an eight-volume Mercury Study Report to Congress. The eight volumes are as follows:

- I. Executive Summary
- II. An Inventory of Anthropogenic Mercury Emissions in the United States
- III. Fate and Transport of Mercury
- IV. An Assessment of Exposure to Mercury in the United States
- V. Health Effects of Mercury and Mercury Compounds
- VI. An Ecological Assessment for Anthropogenic Mercury Emissions in the United States
- VII. Characterization of Human Health and Wildlife Risks from Mercury Exposure in the United States
- VIII. An Evaluation of Mercury Control Technologies and Costs

This volume (Volume V) addresses the potential human health effects associated with exposure to mercury. It summarizes the available human and animal studies and other supporting information relevant to the toxicity of mercury and mercury compounds in humans. It also summarizes U.S. EPA's current overall assessments of hazard and quantitative dose-response for various categories of toxic effects. This volume presents data relevant to assessment of potential effects on human health for elemental mercury, inorganic mercury and methylmercury. Organic mercury compounds other than methylmercury are generally not considered in this volume. Chapter 2 discusses the toxicokinetics of mercury, including information on absorption, distribution, metabolism and excretion. Chapter 3 is a summary of the toxicity literature for mercury. It is organized into three main subsections, corresponding to elemental mercury, inorganic mercury and methylmercury. Within each of these subsections, the study data are presented according to the effect type (e.g., death, renal toxicity, developmental toxicity, cancer). For each effect type, separate summary tables in similar formats are used to present the available data from human epidemiological studies, human case studies, and animal studies.

Chapter 6, Hazard Identification and Dose-Response Assessment, presents U.S. EPA's assessments of the hazard presented by various forms of mercury and, where possible, the quantitative dose-response information that is used in risk assessments of mercury. Chapters 4 and 5 briefly discuss populations with increased susceptibility to mercury and interactions between exposure to mercury and other substances. Ongoing research and research needs are described in Chapter 7, and Chapter 8 lists the references cited. Appendix A documents the dose conversion equations and factors used. Appendix B consists of RfD, RfC and cancer risk summaries for U.S. EPA's Integrated Risk Information System (IRIS). Appendix C lists the participants of a U.S. EPA-sponsored workshop on mercury issues held in 1987. Appendix D presents an analysis of uncertainty and variability in the methylmercury human effects threshold estimate.

soluble salt mercuric sulfide is not absorbed from the gastrointestinal tract as well as the more soluble mercuric chloride salt (Sin et al. 1983).

Mercurous salts in the form of calomel (long in use as a therapeutic agent) are insoluble in water and are poorly absorbed from the gastrointestinal tract (Clarkson 1993a). Long term use of calomel, however, has resulted in toxicity in humans (Davis et al. 1974).

#### 2.1.2.3 Dermal

Dermal absorption of mercuric chloride has been observed in treated guinea pigs (Skog and Wahlberg 1964). Approximately 2–3% of an applied dose was absorbed during a 5-hour period. Absorption was measured both by disappearance of the applied compound and by appearance in kidney, liver, urine and blood.

### 2.1.3 Methylmercury

#### 2.1.3.1 Inhalation

Inhaled methylmercury vapors are absorbed through the lungs. Fang (1980) did not measure percent absorbed but showed a correlation between tissue mercury levels and both exposure level and duration in rats exposed to radioactively labelled methylmercury vapor.

#### 2.1.3.2 Oral

Methylmercury is efficiently absorbed from the gastrointestinal tract. Approximately 95% of methylmercury in fish ingested by volunteers was absorbed from the gastrointestinal tract (Aberg et al. 1969; Miettinen 1973). Similarly, when radiolabeled methylmercuric nitrate was administered in water to volunteers, uptake was greater than 95% (Aberg et al. 1969).

Reports of the percentage of absorbed methylmercury distributed to the blood range from 1% to 10%. Following the ingestion of a single meal of methylmercury-contaminated fish, Kershaw et al. (1980) found that blood accounted for 5.9% of absorbed methylmercury, while Miettinen et al. (1971) found an initial value of 10%, decreasing to about 5% over the first 100 days. In a population that chronically ingested fish with high methylmercury levels, approximately 1% of the absorbed dose was distributed to the blood (Sherlock et al. 1982).

#### 2.1.3.3 Dermal

Dermal absorption of the methylmercuric cation ( $\text{CH}_3\text{Hg}^+$ ) (as the dicyandiamide salt) has also been observed in treated guinea pigs (Skog and Wahlberg 1964). Approximately 3–5% of the applied dose was absorbed during a 5-hour period. Absorption was measured both by disappearance of the applied compound and by appearance in kidney, liver, urine and blood.





barrier is incomplete in fetal and neonatal animals, which may also contribute to the increased mercury levels in immature brain. For example, the higher levels in the neonatal brain of rats and guinea pigs are believed to be associated with the decrease in renal sequestration of the mercuric ion (Jugo 1976; Yoshida et al. 1989). The higher levels observed in the livers of rat neonates may be attributable to increased distribution to organs other than the kidney as well as to higher levels of neonatal hepatic metallothionein (Daston et al. 1986).

### 2.2.3 Methylmercury

Methylmercury is distributed throughout the body, easily penetrating the blood-brain and placental barriers in humans and animals (Clarkson 1972; Hansen 1988; Hansen et al. 1989; Nielsen and Andersen 1992; Soria et al. 1992; Suzuki et al. 1984). By contrast with elemental mercury, studies in rats indicate that methylmercury transport into tissues is mediated by the formation of a methylmercury-cysteine complex (Aschner and Aschner 1990; Tanaka et al. 1991, 1992; Kerper et al. 1992). The complex is structurally similar to methionine and is transported into cells via a widely distributed neutral amino acid carrier protein. Methylmercury associates with water-soluble molecules (e.g., proteins) or thiol-containing amino acids because of the high affinity of the methylmercuric cation ( $\text{CH}_3\text{Hg}^+$ ) for the sulfhydryl groups ( $\text{SH}$ ). Complexes of methylmercury with cysteine have been identified in blood, liver and bile of rats (Aschner and Aschner 1990).

Al-Shahristani and Shihab (1974) calculated a “biological half-life” of methylmercury in a study of 48 male and female subjects who had ingested seed grain contaminated by organic mercurials. The half-life ranged from 35 to 189 days with a mean of 72 days; it was determined from distribution of mercury along head hair.

The blood half-life is 49–164 days in humans (Aberg et al. 1969; Miettinen et al. 1971) and 10–15 days in monkeys (Rice et al. 1989). Smith et al. (1994) determined a blood half-life of 32–60 days in a study of seven adult males given i.v. methylmercury. In the blood, methylmercury is found predominantly in the red blood cells (Kershaw et al. 1980; Thomas et al. 1986). In humans, the ratio of red blood cell methylmercury to plasma methylmercury is approximately 20:1. This ratio varies in animal species; the ratio is approximately 20:1 in primates and guinea pigs, 7:1 in mice, greater than 100:1 in rats and 42:1 in cats (Hollins et al. 1975; Magos 1987).

The clinical significance of the differences in the distribution of various forms of mercury in the blood is that it permits diagnosis of the type of mercury to which an individual has been exposed. Short-chain alkyl mercury compounds such as methylmercury or ethyl mercury are very stable in the body, whereas long-chain compounds may be metabolized over time to the mercuric ion. The mercury distribution in the blood, therefore, may shift from a distribution characteristic of methylmercury to one more suggestive of inorganic mercury (Berlin 1986; Gerstner and Huff 1977).

Mercury has been found in the umbilical cord of human newborns at levels comparable to maternal blood levels (Grandjean et al. 1992a). For lactating mothers, the clearance of mercury from the blood appears to be faster than for non-lactating women. Lactating individuals have a blood half-life of 42 days compared to 75 days for non-lactating females among a group of people who had consumed contaminated seed grain (Greenwood et al. 1978). This finding may be due to excretion of mercury via the milk, increased food intake by mothers (which enhances biliary excretion) and/or altered hormonal patterns in lactating mothers (which affect the excretion pattern).

Methylmercury transport across the blood-brain barrier in rats may involve an amino acid carrier (Kerper et al. 1992). Following acute exposure to methylmercury, most of the mercury in the brain is in the organic form; however, with chronic exposures, a greater amount of the mercury in the brain is in the inorganic form, suggesting that the rate of demethylation increases with long-term exposure (Aschner and Aschner 1990). Rice (1989a, 1989b) demonstrated that tissue half-life in the brain may be significantly longer than the blood half-life for methylmercury.

The bioaccumulation of methylmercury can be affected by age and sex (Thomas et al. 1982, 1986, 1988). After administration of methylmercury to rats, the females had higher peak levels of mercury in the kidneys, primarily as methylmercury, compared to the males; inorganic mercury levels did not differ significantly between the sexes (Thomas et al. 1986). Accumulation of mercury in the body is also found to be higher in neonatal rats (Thomas et al. 1988) than in adult rats (Thomas et al. 1982). Ten days after administration of methylmercury, 94% of the dose was still detected in neonates while  $\approx 60\%$  was retained in adults (Thomas et al. 1988). The longer retention of mercury in the neonates may be attributed to various factors including the high amount of mercury accumulated in the pelt of the neonates due to lack of clearance (Thomas et al. 1988) and the lack of a fully developed biliary transport system in the neonates (Ballatori and Clarkson 1982).

## **2.3 Metabolism**

### **2.3.1 Elemental Mercury**

Elemental mercury dissolved in the blood is rapidly oxidized in red blood cells to mercuric mercury by catalase in the presence of hydrogen peroxide (Halbach and Clarkson 1978). Catalase is found in many tissues, and oxidation by this pathway probably occurs throughout the body (Nielsen-Kudsk 1973). The pathway is saturable, however, and hydrogen peroxide production is the rate-limiting step (Magos et al. 1989). Blood and tissue levels of mercuric mercury following exposure to high concentrations of elemental mercury are, therefore, lower than would be expected based on levels observed following exposure to low levels.

### **2.3.2 Inorganic Mercury**

Several investigators have observed exhalation of elemental mercury vapor after oral administration of mercuric mercury to rats and mice, indicating that mercuric mercury in the body can be reduced to elemental mercury (Clarkson and Rothstein 1964; Dunn et al. 1981a, 1981b; Sugata and Clarkson 1979). The reduction of mercuric ion to elemental mercury may occur via cytochrome c, NADPH and NADH, or a superoxide anion produced by the xanthine-xanthine oxidase system (Ogata et al. 1987). There is no evidence that mercuric mercury is methylated to form methylmercury in mammalian cells. The studies of Rowland et al. on the intestinal flora of the Wistar rat show that microbes are responsible for at least a portion of mercuric chloride methylation in the gut.

Mercurous mercury is unstable in biological fluids and rapidly disassociates to one molecule of elemental mercury and one ion of mercuric mercury (Clarkson 1972).

### **2.3.3 Methylmercury**

Methylmercury in the body is relatively stable and is only slowly demethylated to form mercuric mercury in rats (Norseth and Clarkson 1970). The demethylation appears to occur in tissue macrophages (Suda and Takahashi 1986), intestinal microflora (Nakamura et al. 1977; Rowland et al. 1980) and fetal

liver (Suzuki et al. 1984). *In vitro* demethylation has been reported to involve hydroxyl radicals produced by cytochrome P-450 reductase (Suda and Hirayama 1992) or hypochlorous acid scavengers (Suda and Takahashi 1992). Organic mercury compounds with longer alkyl chains are more readily metabolized over time to the mercuric ion (Berlin, 1986).

Methylmercury metabolism may be related to the latent or silent period observed in epidemiological studies from two methylmercury poisonings. During the latent period, both during and after the cessation of exposure, the patient feels no untoward effects. It is possible that a number of biochemical changes may take place in parallel during this period, and some may not be causatively related to the clinical outcome. Ganther (1978) has hypothesized that the carbon-mercury bond in methylmercury undergoes homolytic cleavage to release methyl free radicals. The free radicals are expected to initiate a chain of events involving peroxidation of lipid constituents of the neuronal cells. The onset of symptoms is delayed for the period of time that cellular systems are able to prevent or repair effects of lipid peroxidation. When the cellular defense mechanisms are overwhelmed, rapid and progressive degeneration of the tissue results. In the Iraqi poisoning incident, the latent period before toxic signs were noted varied from a matter of weeks to months. By contrast, in the Japanese poisoning incident, the latency was as long as a year or more. The difference in duration of the latent period may in part be due to the presence of selenium in the fish ingested by the Japanese population. The role of selenium in mercury toxicity is discussed further in Chapter 5.

## **2.4 Excretion**

### **2.4.1 Elemental Mercury**

Excretion of mercury after exposure to elemental mercury vapor may occur via exhaled air, urine, feces, sweat and saliva. The pattern of excretion of elemental mercury changes as elemental mercury is oxidized to mercuric mercury. During and immediately after an acute exposure, when dissolved elemental mercury is still present in the blood, glomerular filtration of dissolved mercury vapor occurs, and small amounts of mercury vapor can be found in the urine (Stopford et al. 1978). Mercury vapor present in the blood may also be exhaled; human volunteers exhaled approximately 7% of the retained dose within the first few days after exposure (Hursh et al. 1976). The half-life for excretion via the lungs is approximately 18 hours. Approximately 80% of the mercury accumulated in the body is eventually excreted as mercuric mercury. As the body burden of mercury is oxidized from elemental mercury to mercuric mercury, the pattern of excretion becomes more similar to mercuric mercury excretion. The majority of the excretion of mercuric mercury occurs in the feces and urine (Cherian et al. 1978). During the first few days after exposure of humans to mercury vapor, approximately four times more mercury was excreted in the feces than in the urine (Cherian et al. 1978). With time, as the relative mercury content of the kidneys increases, excretion by the urinary route also increases (Rothstein and Hayes 1964). Tissue levels of mercury decrease at different rates, but the half-life for excretion of whole-body mercury in humans (58 days) is estimated to be approximately equal to the half-life of elimination from the kidneys (64 days), where most of the body burden is located (Hursh et al. 1976). Excretion via the urine may be increased if mercury-induced damage of the renal tubular epithelium has happened and exfoliation of damaged mercury-containing cells occurs (Magos 1973).

Excretion via sweat and saliva are thought to contribute only minimally to total excretion under normal circumstances. In workers who have perspired profusely, however, the total amount of mercury excreted in the sweat during 90 minutes ranged from 50% to 200% of that found in a 16-hour composite sample of urine (Lovejoy et al. 1974).

#### 2.4.2 Inorganic Mercury

Because of the poor absorption of orally administered mercuric mercury, the majority ( $\approx 85\%$ ) of an ingested dose in humans is excreted in the feces within a few days after administration (Miettinen 1973). Hall et al. (1994) showed that for five adult male volunteers given i.v. mercuric nitrate and evaluated for 70 days, 6.3-35% of the dose was excreted in urine and 17.9-38.1% in feces. For absorbed inorganic mercury, the half-life for excretion has been estimated to be  $\approx 40$  days (Rahola et al. 1973) and 67 days with a range of 49-96 days (Hall et al. 1994). Information on the routes of excretion for absorbed inorganic mercury are limited, but excretion would be expected to be similar to that of inorganic mercury formed in rats by the oxidation of elemental mercury (Rothstein and Hayes 1964). The majority of absorbed inorganic mercury is excreted in the urine (Berlin 1986).

Glomerular filtration is not thought to contribute substantially to urinary excretion of mercuric mercury (Cherian et al. 1978). Rather, mercuric mercury is excreted in the urine primarily as sulfhydryl conjugates (with cysteine or N-acetylcysteine) actively transported into the tubular lumen. Urinary levels correlate with renal mercury concentrations rather than blood mercury levels.

Fecal excretion of mercury occurs as the result of excretion in the saliva, secretion through the epithelium of the small intestines and colon and secretion in the bile (Berlin 1986). Secretion of mercuric mercury in the bile is believed to result from active transport of a mercury-glutathione complex across the canalicular membrane via the glutathione carrier (Ballatori and Clarkson 1982).

Mercuric mercury may also be excreted in breast milk during lactation (Yoshida et al. 1992). The levels in breast milk are proportional to the plasma content. In maternal guinea pigs, milk levels were approximately half of that found in plasma. After termination of exposure, however, mercury levels in milk decreased at a slower rate than plasma mercury levels.

#### 2.4.3 Methylmercury

Like inorganic mercury, methylmercury has a relatively long half-life of approximately 70–80 days in the human body (Aberg et al. 1969; Bernard and Purdue 1984; Miettinen 1973). Recently a shorter half-life of 44 days was estimated by Smith et al. (1994) in their study of seven adult males treated i.v. with methylmercury. In this study methylmercury and inorganic mercury concentrations in blood and excreta were determined separately based on differential extractability into benzene. The predominant species in the blood was methylmercury; there was no detectable methylmercury in the urine.

The long half-life of methylmercury in the body is due, in part, to reabsorption of methylmercury secreted into the bile (hepato-biliary cycling) (Norseth and Clarkson, 1971). In this cycle, methylmercury forms a complex with glutathione in the hepatocyte, and the complex is secreted into the bile via a glutathione carrier protein (Clarkson, 1993b). The methylmercury-glutathione complex in the bile may be reabsorbed from the gallbladder and intestines into the blood. When microorganisms found in the intestines demethylate methylmercury to form mercuric mercury, this cycle is broken, and fecal excretion of mercury from methylmercury occurs (Rowland et al. 1980). Mercuric mercury is poorly absorbed from the intestines, and that which is not reabsorbed is excreted in the feces. In humans, approximately 90% of the absorbed dose of methylmercury is excreted in the feces as mercuric mercury. Excretion via the urine is minor but slowly increases with time; at 100 days after dosing, urinary excretion of mercury accounted for 20% of the daily amount excreted. The urinary excretion of mercury may reflect the deposition of demethylated mercury in the kidneys and its subsequent excretion.

In animals, the predominant route of methylmercury elimination also is the feces (Farris et al. 1993; Hollins et al. 1975; Thomas et al. 1987). As in humans, biliary excretion of methylmercury and its demethylation in gastrointestinal flora have been reported in rats (Farris et al., 1993). After a single oral dose of methylmercury, the major elimination route was the feces (65% of the administered dose as inorganic mercury and 15% of the administered dose as methylmercury) and the minor route was urine (1% of the administered dose as inorganic mercury and 4% of the administered dose as methylmercury) (Farris et al. 1993).

In rat and monkey neonates, excretion of methylmercury is severely limited (Lok 1983; Thomas et al. 1982). In rats dosed prior to 17 days of age, essentially no mercury was excreted (Thomas et al. 1982). By the time of weaning, the rate of excretion had increased to adult levels. The failure of neonates to excrete methylmercury may be associated with the inability of suckling infants to secrete bile (Ballatori and Clarkson 1982) and the decreased ability of intestinal microflora to demethylate methylmercury during suckling (Rowland et al. 1977).

Methylmercury is also excreted in breast milk (Bakir et al. 1973; Sundberg and Oskarsson 1992). The ratio of mercury in breast milk to mercury in whole blood was approximately 1:20 in women exposed to methylmercury via contaminated grain in Iraq between 1971 and 1972 (Bakir et al. 1973). Evidence from the Iraqi poisoning incident also showed that lactation decreased blood mercury clearance half-times from 75 days in males and nonlactating females to 42 days in lactating females; the faster clearance due to lactation was confirmed in mice (Greenwood et al. 1978). In mice, of the total mercury in the breast milk, approximately 60% was estimated to be methylmercury. Skerfving (1988) has found that 16% of mercury in human breast milk is methylmercury. Studies in animals indicate that the mercury content of breast milk is proportional to the mercury content of plasma (Sundberg and Oskarsson, 1992; Skerfving, 1988).

## **2.5 Biological Monitoring**

This section describes the various biological media most frequently used when assessing mercury exposure. In addition, this section describes the available analytical methods for measuring mercury in biological samples. Reference values for mercury in standard biological media from the general population are shown in Table 2-1. These values represent total mercury, not individual mercury species. For hair and blood, these have been indexed to fish consumption as the most common route of exposure in humans.

### **2.5.1 Elemental Mercury**

Blood and urinary mercury are common to assess occupational mercury exposure.

#### **2.5.1.1 Blood**

In workers chronically exposed to mercury vapor, a good correlation was observed between intensity of mercury vapor exposure and levels of mercury in the blood at the end of a workshift (Roels et al. 1987). The usefulness of blood as a biomarker for exposure to elemental mercury depends on the time elapsed since exposure and the level of exposure. For recent, high-level exposures, whole blood analysis may be used to assess exposure (Clarkson et al. 1988). Mercury in the blood peaks rapidly, however, and decreases with an initial half-life of approximately two to four days (Cherian et al. 1978). Thus, evaluation of blood mercury is of limited value if a substantial amount of time has elapsed since exposure. Also, dietary methylmercury contributes to the amount of mercury measured in blood. At low

levels of elemental mercury exposure, the contribution of dietary methylmercury to the total blood mercury may be high relative to that of the inhaled mercury, limiting the sensitivity of this biomarker. Several studies have

**Table 2-1**  
**Reference Values for Total Mercury Concentrations in Biological Media for the General Population**

Medium	Mercury Concentration	Reference
Whole blood	1–8 µg/L 2 µg/L	WHO (1990) Nordberg et al. (1992) Brune (1991)
Fish consumption:		
No fish meals	2.0 µg/L	
2 meals/week	4.8 µg/L	
2–4 meals/week	8.4 µg/L	
more than 4 meals/week	44.4 µg/L	
Urine	4–5 µg/L	WHO (1990)
Scalp hair	2 µg/g	WHO (1990) Airey (1983)
Fish consumption:		
once/mo	1.4 µg/g	
once/2 wk	1.9 µg/g	
once/wk	2.5 µg/g	
once/day	11.6 µg/g	

separated whole blood into its plasma and erythrocyte fractions in order to evaluate potential confounding factors due to the presence of methylmercury (95% of methylmercury is found in the red blood cell). Some published values indexed to fish consumption are in Table 2-1.

#### 2.5.1.2 Urine

Urinary mercury is thought to indicate most closely the mercury levels present in the kidneys (Clarkson et al. 1988). For most occupational exposures, urinary mercury has been used to estimate exposure. In contrast to blood mercury levels, urinary mercury peaks approximately 2–3 weeks after exposure and decreases at a much slower rate with a half-life of 40–60 days for short-term exposures and 90 days for long-term exposures (Barregard et al. 1992; Roels et al. 1991). The urine remains, therefore, a more appropriate indicator for longer exposures than blood samples. As little dietary methylmercury is excreted in the urine, the contribution of ingested methylmercury to the measured levels is not expected to be high. Good correlations have been observed between urinary mercury levels and air levels of mercury vapor; however, these correlations were obtained after correcting urinary mercury content for variations in the urinary excretion rate (using urinary creatinine content or specific gravity) and after standardizing the amount of time elapsed after exposure (Roels et al. 1987). Such steps are necessary because considerable intra- and interindividual variability has been observed in the urinary excretion rate (Barber and Wallis 1986; Piotrowski et al. 1975). Even when such precautions are taken, intraindividual variability remains at ≈18% (Barregard et al. 1992; Roels et al. 1987).

#### 2.5.1.3 Exhaled Air

Exhaled air has been suggested as a possible biomarker of exposure to elemental mercury vapor because a portion of absorbed mercury vapor is excreted via the lungs. Excretion by this route has a half-

life of approximately 18 hours (Hursh et al. 1976). At low levels of exposure, however, mercury vapor released from dental amalgam may contribute substantially to the measured amount of mercury.

#### 2.5.2 Inorganic Mercury

No information was identified in the literature that specifically assessed biological indicators for inorganic mercury exposure. The information presented above for detection of mercury in blood and urine after occupational exposure to elemental mercury vapor should also apply to inorganic mercury exposures because elemental mercury vapor is rapidly converted to mercuric mercury after absorption.

#### 2.5.3 Methylmercury

Blood and scalp hair are the primary indicators used to assess methylmercury exposure.

##### 2.5.3.1 Blood

Because methylmercury freely distributes throughout the body, blood is a good indicator medium for estimating methylmercury exposure. Because an individual's intake may fluctuate, blood levels may not necessarily reflect mercury intake over time (Sherlock et al. 1982; Sherlock and Quinn, 1988). At steady state, blood levels have been related to dose by the following equation (Kershaw et al. 1980):

$$d = \frac{C \times b \times V}{A \times f}$$

Where:

C = concentration in blood (expressed in  $\mu\text{g/L}$ )

V = volume of blood (expressed as L)

b = the kinetic rate constant ( $\text{day}^{-1}$ )

A = absorption rate (unitless)

F = fraction of dose that is present in blood

d = intake ( $\mu\text{g/day}$ )

It is useful to measure blood hematocrit and mercury concentrations in both whole blood and plasma. From these data, the red blood cell to plasma mercury ratio may be determined, and interference from exposure to high levels of elemental or inorganic mercury may be estimated (Clarkson et al. 1988).

##### 2.5.3.2 Scalp Hair

Scalp hair can also be a good indicator medium for estimating methylmercury exposure (Phelps et al. 1980). Methylmercury is incorporated into scalp hair at the hair follicle in proportion to its content in blood. The hair-to-blood ratio in humans has been estimated as approximately 250:1 expressed as  $\mu\text{g Hg/g hair}$  to  $\text{mg Hg/L blood}$ , but some difficulties in measurements, interindividual variation in body burden, differences in hair growth rates, and variations in fresh and saltwater fish intake have led to varying estimates (Birke et al. 1972; Skerfving 1974). Once incorporated into the hair, the methylmercury is stable, and, therefore, gives a longitudinal history of blood methylmercury levels



(Phelps et al. 1980; WHO, 1990). Analysis of hair mercury levels may be confounded by adsorption of mercury vapor onto the hair strands (Francis et al. 1982).

#### 2.5.4 Methods of Analysis for Measuring Mercury in Biological Samples

The most common methods used to determine mercury levels in blood, urine and hair of humans and animals include atomic absorption spectrometry (AAS), neutron activation analysis (NAA), X-ray fluorescence (XRF) and gas chromatography (GC). Table 2-2 identifies the major characteristics of these methods.

**Table 2-2**  
**Analytical Methods for the Detection of Mercury in Biological Samples**

Method	Able to Distinguish Methylmercury?	Detection Limit (ppm)	References
NAA	No	0.1	Byrne and Kosta (1974) WHO (1976)
AAS	No No*	2 PPB range	Hatch and Ott (1968) Magos and Clarkson (1972)
GC — Electron capture	Yes	1.0	Von Burg et al. (1974) Cappon and Smith (1978)
XRF	No	"low ppm"	Marsh et al. (1987)

\* The Magos and Clarkson method estimates methylmercury by subtracting the inorganic mercury content from the total mercury content.

## 2.6 **Studies on Pharmacokinetic Models**

### 2.6.1 Introduction

Pharmacokinetic modeling is a process by which administered dose, such as the amount of a compound instilled into the body via inhalation, ingestion or parenteral route is used to estimate measures of tissue dose which may not always be accessible to measurement by direct experimentation. A pharmacokinetic model is employed to predict relevant measures of tissue dose under a wide range of exposure conditions. In practice, the pharmacokinetic models used may incorporate features such as compartmental analysis and physiologically-based models.

Reports available on the *in vivo* distribution of several types of mercury compounds provide different physiokinetic relationships between the structure of mercury compounds and their behavior in living organisms because the studies reported have been carried out under different experimental conditions. Takeda et al. (1968) reported that in the rat, alkyl mercury compounds such as ethylmercuric chloride and butylmercuric chloride were excreted more slowly and were retained in higher concentration for a longer time in the body than mercuric chloride and phenylmercuric chloride. The distribution of mercury in the brain was found to depend on the structure of the mercury compounds; relatively high accumulation was observed for ethyl and n-butyl mercury compounds. Sebe and Itsuno (1962) reported that after oral administration methyl-, ethyl-, and n-propylmercury compounds were neurotoxic to rats;

n-butylmercury was not neurotoxic and thus presumably did not cross the blood-brain barrier. By contrast, Suzuki et al. (1963, 1964) reported that ethylmercuric acetate and n-butylmercuric acetate had similar patterns of distribution when subcutaneously administered to mice.

#### 2.6.2 Inorganic mercury

Few controlled laboratory studies of pharmacokinetics of mercury in humans have been published (Hursh et al. 1976, Rahola et al. 1973). Rahola et al. (1973) examined mercury absorption and elimination after oral administration of mercuric nitrate to five male and five female volunteers, and reported very low and variable rate of gastrointestinal absorption (8 to 25% dose). They reported a half-time for inorganic mercury in human red blood cells of 16 days and whole body of 46 (32–60) days in males and somewhat lower values in females. Hursh et al. (1976) found half-times for mercury clearance from the body of 58 (35–90) days after exposure to mercury vapor. Whole body clearance from the Rahola et al. (1973) study appeared biphasic with half-times of 2.3 days for the fast compartment and 42 (39–45) days for the slow compartment.

Low and variable rates of absorption of orally administered inorganic mercury in the Rahola et al. (1973) study prompted Hall et al. (1994) to examine distribution of intravenously administered inorganic mercury in human volunteers. In order to describe retention of mercury after transient distributional effects, a one-compartment model was fit to the blood and body burden data after day 10, assuming first order kinetics. The half-lives observed in the single compartment model for blood and body burden were 30 (19.7–65.6 days) and 67 (48.6–95.5 days) days, respectively. The authors attempted closer agreement between observed and predicted values by structuring a multicompartment model. Measured mercury concentrations in blood, urine, feces, and whole body radioactive levels of mercury were used in an *a posteriori* fashion to develop a model comprising six blood compartments, one compartment each for feces and urine and a delayed compartment for feces. Inter-subject variability (temporal pattern of blood mercury) and the existence of a kinetically distinct plasma pool (three distinct compartments) for mercury resulted in equivocal predictions for blood, urine and feces; whether these findings point to uncertainties of measurement of body burden or incomplete collection of excreta or suggest other pathways of excretion, such as exhalation or sweating, is unknown. The authors concluded that this type of complex pattern of blood kinetics, although unusual, is not without precedent. Four kinetically distinct plasma pools of selenium has been reported after oral dosing with a stable isotopic tracer (Patterson and Zech 1992). Hall et al. (1994) noted that the apparently linear kinetics observed for the small tracer doses of i.v. inorganic mercury would likely change with toxicity associated with larger or more frequent doses.

#### 2.6.3 Methylmercury

Methylmercury is structurally the simplest of the organic mercurials; it bioaccumulates in certain species of fish, some of which are important human and wildlife foods. In order to elucidate the mechanisms that influence the pharmacokinetics of both methylmercury and mercuric mercury and to extrapolate further both intra- and inter-species extrapolation of experimental data for these toxins, Farris and associates (1993) developed a physiological pharmacokinetic model for methylmercury and its metabolite, mercuric mercury. This was done in growing rats dosed orally with labeled methylmercury over a period of 98 days. Mercuric mercury accounted for less than 0.5% of total activity. Extensive sets of metabolism and distribution data were collected to understand the processes that influence the pharmacokinetics of both methylmercury and mercuric mercury. The model consisted of nine lumped compartments, each of which represented a major site of mercury accumulation, distribution or elimination. The carcass served as a residual compartment, which included all tissues and organs not

separately incorporated into the model. Model simulations in this study were made with experimentally determined concentrations of both inorganic and methylmercury in blood, brain, kidney and liver. The data showed bidirectional and symmetric transport of both chemical species between blood and tissues with relatively slow movement into and out of the brain. Some key parameters remained uncertain; for example, the rate constant for demethylation is one of the most critical in adopting the model to other species. This model, however, established a foundation for more complete understanding of methylmercury pharmacokinetics. With further refinements, it could be applied to other species including humans. To characterize health hazard from dietary methylmercury better, one needs to understand the distribution of methylmercury in the body, the extent to which it accumulates and the rate at which it is eliminated. Farris et al. (1993) noted that following methylmercury dosing there was a buildup of inorganic mercury in tissues and that excreted mercury was predominantly mercuric; methylmercury behaved as a single body pool, while mercuric mercury was handled differently in different tissues.

Smith and associates (1994) made further refinements to the Farris et al. (1993) model. They reported a multicompartiment pharmacokinetic model for methylmercury and mercuric mercury in seven human volunteers. This model simulated the long-term disposition of methylmercury and inorganic mercury in humans following a single i.v. dose of radio-labeled methylmercury. This was a tracer amount to avoid toxic or saturation effects. The behavior of both methylmercury and inorganic mercury in the body was modeled with the simplest compartmental model which fitted the data; blood, urine and feces data were used to fit the model. In this model the tracer dose was delivered to the first blood compartment and subsequently distributed to two extra-vascular methylmercury compartments; two distinct compartments (urine and feces) for inorganic mercury were added features. This five-compartment model showed that inorganic mercury accumulated in the body and at longer times was the predominant form of mercury present. The biological half-life of methylmercury in the body was calculated to be 44 days, and 1.6% of the body burden was lost each day by both metabolism and excretion.

To characterize neurological impairments of prenatal methylmercury exposure in children, Gearhart and associates (1995) applied a more sophisticated multispecies pharmacokinetic model and statistical dose-response analysis to an epidemiological study of a large population in New Zealand (Kjellstrom et al. 1989) which featured relatively constant chronic exposure to methylmercury in fish. The model for methylmercury in this study consisted of an adult with 11 compartments representing both organ-specific and lumped tissues; eight compartments represented transport of methylmercury as flow-limited, and three other compartments represented transport as diffusion-limited. The flow-limited compartments were plasma, kidney, richly perfused, slowly perfused, brain-blood, placenta, liver and gut compartments; RBC, brain and fetus were the diffusion-limited compartments. There were also four other compartments in the model which were involved in methylmercury uptake and elimination: methylmercury in the urine; and methylmercury and inorganic mercury in the hair, feces and the intestinal lumen. The fetal sub-model for methylmercury consisted of four compartments: fetal plasma, RBCs, brain and the remaining fetal body. This modeling effort was designed to create a multispecies model that would be amenable to simulation of the kinetics of methylmercury by simply changing the species-specific parameters. Unlike Farris et al. (1993), separate red blood cell and plasma compartments were used to predict changes in kinetics of methylmercury across species due to differences in the red blood cell/plasma ratio. Different pharmacokinetic parameters, such as tissue/blood partition coefficients and volume distributions for humans, rats and monkeys, were taken from different studies published in the current literature. The authors provided a benchmark dose on results of a battery of neurobehavioral tests in 6-year-old children prenatally exposed to methylmercury in seafood. Their calculations suggested a NOAEL of 17 ppm Hg in maternal hair for the most sensitive

neurological event in children. The analysis of the pharmacokinetic model indicated that the fetal brain concentrations of methylmercury at this NOAEL were on the order of 50 ppb and were associated with maternal dietary intakes of methylmercury ranging from 0.8 to 2.5  $\mu\text{g/kg-day}$ . These analyses provided support to the Iraqi data used in the development of the RfD for methylmercury, presented in the risk assessment chapter (Chapter 6) of this volume.

#### 2.6.4 Discussion

Both simple and complex multi-compartment models have been reported by Hall et al. (1994), Farris et al. (1993), Smith et al. (1994) and Gearhart et al. (1995). The Hall et al. (1994) paper discussed a model which employed inorganic mercury data obtained from human studies; however, temporal patterns of blood mercury and the existence of kinetically distinct plasma pools for mercury present uncertainties which limit the use of this model in risk assessment. Farris et al. (1993) reported a multicompartiment model using data obtained from rats exposed to methylmercury in diets over a period of 98 days. They observed a buildup of inorganic mercury in tissues and the conversion of methylmercury to inorganic mercury could not be accurately predicted by whole-body counting, which was also subjected to errors from low sensitivity and the inability to compensate for geometric changes due to redistribution of methylmercury or translocation of inorganic mercury to its target tissues. Smith and associates (1994) refined this model and presented a multicompartiment model using data obtained from humans given a single i.v. dose of methylmercury. Uncertainties, however, persist in prediction of methylmercury exposures in food. Since methylmercury causes subtle neurotoxicity in children, this model may not be predictive of exposure in children. This potential neurotoxicity observed in prenatally exposed children prompted Gearhart et al. (1995) to develop multicompartiment adult and fetal model using data from rat, monkey and humans. This model was applied to an epidemiology study on which benchmark dose analysis was used to better characterize the dose-response information rather than the traditional NOAEL approach. In the risk assessment chapter of this volume, U.S. EPA utilizes a benchmark dose approach for setting the RfD for methylmercury. A multispecies compartment model discussed in the Gearhart et al. (1995) report may provide a viable approach because it can use data from both adults and neonates. This approach can use adult and neonatal effects data from several animal and human studies to account for evidences of non-linearities in dose-responses. Research is needed to reduce uncertainties in racial, ethnic, and cultural differences which exist in epidemiological studies.



**Table 3-59**  
**Neurotoxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Rat/Wistar/ 10 F	0-12 or 12-20 d, 1x/d (gavage)	2, 4 (MMC)*	Hindlimb crossing (LOAEL = 4) after 0-12 days BML not reported	Inouye and Murakami 1975
Rat/Wistar/ 50 F, 50 M	up to 26 mo ad lib in feed	0.002, 0.01, 0.05, 0.25 (MMC)*	Ruffled fur, loss of balance, hindlimb crossing, paralysis (LOAEL = 0.25) after 6 mo (males more affected); demyelination of dorsal nerve roots and damage in teased sciatic nerves at 0.25 Avg. BML at 0.25: 115 ppm in blood	Munro et al. 1980
Rat/Charles River/6 M	8 wk 7 d/wk 1 x/d (gavage)	0, 1.6 (MMC)*	Degeneration of dorsal root fiber BML not reported	Yip and Chang 1981
Rat/Wistar/24 M, 18 F	5 d 1 x/d (gavage)	8 (MMC)*	Cerebellar granule cell and dorsal root ganglion cell degeneration; flailing and hind leg crossing following administration of methylmercuric chloride Limitations: Only one level tested; no controls Avg BML: 150,000 µg/L in blood	Magos et al. 1985
Rat/Wistar/15 M	5 x/15 d (gavage)	0, 10 (MMC)*	Granule cell degeneration in cerebellum BML: 60 µg/g dry cerebellar weight	Leyshon and Morgan 1991
Swiss origin Mouse M	28 wk (ad lib drinking water)	1.9, 9.5 (MMC)*	Ataxia; degenerative changes of Purkinje cells; granule cell loss in cerebellum; (LOAEL = 1.9) BML not reported	MacDonald and Harbison 1977
Cat/Breed NS/15-16 both sexes	11 mo (ad lib in feed)	0, 0.015 (MM)	Degeneration of cerebellum and cerebral cortex; necrosis of dorsal root ganglia of kittens fed mercury-contaminated tuna BML not reported	Chang et al. 1974
Cat/Breed NS/8-10 NS	2 yr 7 d/wk (feed)	0.003, 0.008, 0.020, 0.046, 0.074, 0.176 (MMC)*	Impaired hopping reaction; decreased pain sensitivity; degeneration of dorsal root ganglia (LOAEL = 0.046) Avg BML: 9,000 µg/L in blood at 0.046 mg/kg-day	Charbonneau et al. 1976
Monkey/ <i>Macaca fascicularis</i> /1-2 both sexes	36-132 d 1 x/d (feed)	0.02, 0.03, 0.04, 0.07, 0.21	Atrophy of neurons in calcarine cortex; focal degeneration in sural nerves (LOAEL=0.03); ataxic gait, myoclonic seizures at 0.21 mg/kg-day Limitation: small number of animals tested BML: Maximal at 0.03 mg/kg-day of 460 µg/L in blood and 62 µg/g in hair	Sato and Ikuta 1975
Monkey/ <i>Macaca artoides</i> , <i>Macaca nemestrina</i> /2 both sexes	90-270 d 1 x/wk (gavage)	1 for 5 doses, then 0.4, 0.5, 0.6	Tremor; visual impairment (LOAEL = 0.5 mg/kg) Limitations: Small number of animals tested, limited description of effects Avg BML: 2,900 µg/L in blood	Evans et al. 1977

**Table 3-59 (continued)**  
**Neurotoxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Monkey/ <i>Macaca fascicularis</i> /5 exposed, 2 control (sex NS)	3-4 yr 7 d/wk 1 x/d (NS)	0, 0.05 (MMC)*	Spatial visual impairment Limitation: One dose level tested BML: 600-900 µg/L in blood	Rice and Gilbert 1982
Monkey/ <i>Macaca fascicularis</i> /7-8 F	~3 yr 1 x/d (oral route NS)	0, 0.04, 0.06, 0.08 (MMC)*	Slight tremor; motor incoordination; blindness (LOAEL = 0.04) following administration of methylmercury hydroxide; time to onset was 177-395 d Avg BML: 2,030 µg/L in blood at highest dose	Burbacher et al. 1988
Monkey/ <i>Macaca fascicularis</i> /4 M, 1 F exposed, 1 M, 2 F controls	6.5-7 yr 7 d/wk 1 x/d (capsule; gavage)	0, 0.05 (MMC)*	Six years after end of dosing (follow-up study to Rice and Gilbert 1982): decreased fine motor performance; diminished touch and pinprick sensitivity; impaired high frequency hearing (p<0.05) Limitations: small number of animals tested; one dose level tested BML: Not detectable at time of testing	Rice 1989b; Rice and Gilbert 1992

\*MMC = methylmercuric chloride

### 3.3.3.3 Renal

No studies were located regarding the renal toxicity of methylmercury in humans following oral exposure. Renal histopathology and decreased function have been observed following acute or chronic oral exposure of rats and mice to methylmercury. Renal tubule vacuolation was observed in rats receiving 8 mg Hg/kg-day for 5 days (Magos et al. 1985), and decreased phenolsulfonphthalein excretion occurred in male mice receiving a single dose of 16 mg Hg/kg-day or greater and females at 32 mg Hg/kg-day or greater as methylmercuric chloride (Yasutake et al. 1991). Chronic nephropathy, including epithelial degeneration of proximal tubules and interstitial fibrosis, was observed at longer durations (Fowler 1972; Hirano et al. 1986; Mitsumori et al. 1990). Males were more sensitive than females to renal effects (Mitsumori et al. 1990).

**Table 3-60**  
**Renal Toxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Rat/Wistar/3 M, 6 F exposed/16 controls (sex NS)	12 wk ad lib in feed	0, 0.08 (M) 0, 0.09 (F) (MMC)	Cytoplasmic mass in proximal tubule cells Limitation: Only one level tested; small number of treated animals BML not reported	Fowler 1972
Rat/Wistar/24 M, 18 F	5 d 1 x/d (gavage)	8	Renal tubule vacuolation and dilation Limitation: One level tested, no controls Avg. BML: 150,000 µg/L in blood	Magos et al. 1985
Mouse/ICR/60 M, 60 F	26 wk ad lib in feed	0, 0.03, 0.15, 0.72 (M); 0.02, 0.11, 0.62 (F)	Toxic epithelial degeneration of renal proximal tubules (LOAEL = 0.62 F; 0.72 M) BML not reported	Hirano et al. 1986
Mouse/ B6C3F <sub>1</sub> /60 M, 60 F	104 wk ad lib in feed	0, 0.03, 0.14, 0.68 (M); 0.03, 0.13, 0.6 (F) (MMC)	Chronic nephropathy (epithelial cell degeneration, regeneration of proximal tubules, interstitial fibrosis) in males at ≥0.14 and in females at 0.60 (p<0.01) BML not reported	Mitsumori et al. 1990
Mouse/ C57BL/6 M, 6 F	Once (gavage)	4, 8, 16, 24, 32, 40 (MMC)	Decreased phenolsulfonphthalein excretion and increased serum creatinine in males (LOAEL = 16 in males, 32 in females); swollen epithelial cells in proximal tubules Limitation: No statistical analysis; small number of treated animals BML: 2.45 µg/g in kidneys of males and 1.9 µg/g in kidneys of females at 16 mg/kg	Yasutake et al. 1991

#### 3.3.3.4 Cardiovascular

Only one study was located regarding the cardiovascular toxicity of methylmercury in humans. Hook et al. (1954) reported two men with elevated blood pressure after inhalation exposure to organic mercury particulates from seed dressings. Other neurotoxic effects were also present at the time of examination, and one man subsequently died.



**Table 3-61**  
**Cardiovascular Toxicity of Methylmercury in Humans: Case Study**

Species/ No. per Sex	Exposure Duration	Dose (mg/m <sup>3</sup> )	Effects/Limitations/BML	Reference
Human/1 M	3 yr (occup)	NS	Elevated blood pressure Limitations: Case study; concomitant dermal exposure likely BML Range: 500-640 µg/L in urine	Hook et al. 1954

Very little information was located regarding the effects of oral methylmercury exposure on the cardiovascular system. Rats given two daily doses of methylmercuric chloride exhibited decreases in heart rates (Arito and Takahashi 1991). Rats treated with methylmercuric chloride for one month had increased systolic blood pressures beginning 42 days after cessation of dosing (Wakita 1987). This effect persisted for more than a year.

**Table 3-62**  
**Cardiovascular Toxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitation/BML	Reference
Rat/Wistar/10 (sex NS)	23-28 d 7 d/wk (gavage)	0.4, 1.2 (MMC)	Increased systolic pressure beginning 42 d after the end of treatment (p<0.05) BML not reported	Wakita 1987
Rat/Sprague- Dawley/5-6 (sex NS)	2 d 1 x/d (gavage)	12 (MMC)	Decreased heart rate (p<0.05) Limitation: Only one dose tested for this parameter BML: 10 µg/g in brain	Arito and Takahashi 1991

#### 3.3.3.5 Gastrointestinal

No information was located regarding the gastrointestinal toxicity of methylmercury in humans. Only one study was located regarding the gastrointestinal toxicity of methylmercury following oral exposure in animals. Mitumori et al. (1990) reported an increased incidence of stomach ulceration in mice following a 2-year exposure to 0.69 mg Hg/kg-day as methylmercuric chloride in drinking water.

**Table 3-63**  
**Gastrointestinal Toxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Mouse/ B6C3F <sub>1</sub> /60 M, 60 F	104 wk ad lib in feed	0, 0.03, 0.14, 0.69 (M); 0.03, 0.13, 0.6 (F) (MMC)	Stomach ulceration in males at 0.69 (p<0.05) BML not reported	Mitsumori et al. 1990

### 3.3.3.6 Immunological

Suppression of the humoral and cellular immune responses have been observed in animals after oral exposure to methylmercury or methylmercuric chloride. Both decreases in the production of antibody-producing cells and decreased antibody titre in response to inoculation with immune-stimulating agents (such as sheep red blood cells) have been observed (Blakley et al. 1980; Koller et al. 1977; Ohi et al. 1976). Decreases in natural killer T-cell activity have been observed in animals after exposure to methylmercury (Ilback 1991).

**Table 3-64**  
**Immunotoxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Rat/Brown Norway/6 both sexes exposed/22 both sexes/controls	NS x/wk 2 mo	0, 4.8 (MMC)	IgG deposits along the glomerular capillary wall of the kidney, not in arteries, suggestive of an autoimmune disease; no effect seen in controls. Limitation: only one level tested BML not reported	Bernaudin et al 1981
Mouse/ICR/6 M	5 d 1 x/d (gavage)	0.27, 2.7 (MMC)	Decreased production of antibody-producing cells (LOAEL = 2.7; p<0.01). Limitation: small number of animals, only males tested BML not reported	Ohi et al. 1976
Mouse/Swiss/8-10 M	3 wk ad lib in drinking water	0.076, 0.3, 1.52 (MMC)	Decreased production of antibody-producing cells and decreased antibody titer (LOAEL = 0.076; p<0.01). Limitation: small number of animals, only males tested BML not reported	Blakley et al. 1980

**Table 3-64 (continued)**  
**Immunotoxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Mouse/Balb/c CUM/ 8 F	12 wk ad lib in feed	0, 0.5	Reduced natural killer T-cell activity; decreased thymus weight and cell number ( $p < 0.01$ ). Limitation: small number of animals treated, only females tested BML not reported	Ilback 1991
Rabbit/New Zealand white/10 M, 10 F	14 wk 1 x/d in feed	0.04, 0.4, 0.8 (MMC)	Decreased antibody titer (LOAEL = 0.4) (26% of the animals at 0.4 and no controls died by wk 14). Limitations: No statistical analysis BML: 2,240 µg/L in blood at 0.4 mg/kg/d at wk 14	Koller et al. 1977

### 3.3.3.7 Dermal

Al-Mufti et al. (1976) studied the effects of methylmercury in humans who ate contaminated bread; a correlation between bread consumption and a history of rash was reported. No other information was located regarding dermal effects of organic mercury following oral exposure.

**Table 3-65**  
**Dermal Toxicity of Methylmercury in Humans: Epidemiological Study**

Species/ No. per Sex	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Human/415 exposed/1012 controls (sex NS)	≈ 1-3 mo (feed)	NS (MMC)	"History of rash" in 14% of exposed group, compared with <1% of unexposed Limitations: Effects poorly described; no statistical analysis BML not reported	Al-Mufti et al. 1976

### 3.3.3.8 Developmental

Methylmercury readily crosses the placental barrier, and marked developmental toxicity has been observed in both humans and animals after gestational exposures. Infants exposed to methylmercury through the mother's milk or during gestation had elevated blood mercury levels, as did their mothers (Amin-Zaki et al. 1976). Human data from epidemic poisonings that occurred in Japan (Harada 1978) and Iraq (Amin-Zaki et al. 1974), as well as isolated exposures (Snyder and Seelinger 1976) indicate that methylmercury predominantly affects the developing nervous system. Infants born to mothers who ingested fish contaminated with methylmercury from Minamata Bay in Japan between 1953 and 1960

appeared normal at birth but within several months exhibited mental retardation, retention of primitive reflexes, cerebellar symptoms, dysarthria, hyperkinesia, hypersalivation, strabismus and pyramidal symptoms (Harada 1978). Similarly, infants born to mothers who had ingested bread made with seed grain treated with methylmercury-containing fungicides in Iraq during 1971 to 1972 exhibited symptoms ranging from delays in speech and motor development to mental retardation, reflex abnormalities and seizures (Amin-Zaki et al. 1974, 1978). Histopathologic analyses of brain tissues from infants that died in the Iraqi (Choi et al. 1978) and Minamata (Harada 1978) episodes showed atrophy and hypoplasia of the cerebral cortex, corpus callosum and granule cell layer of the cerebellum; dysmyelination of the pyramidal tracts; and/or abnormal neuronal cytoarchitecture characterized by ectopic cells and disorganization of cellular layers.

A number of studies have attempted to evaluate developmental neurotoxicity in populations with elevated methylmercury exposure from consumption of fish as a major component of the diet but for whom massive poisonings have not been reported. Kjellstrom et al. 1989) observed a higher incidence of abnormal scoring on tests designed to assess intelligence and development among children from New Zealand whose mothers had high levels of hair mercury. Also a study by McKeown-Eyssen et al. (1983) of a Cree population from northern Quebec revealed a correlation between maternal exposure (as determined using hair levels) and abnormal muscle tone or reflexes in male children. A dose-response for this effect was not observed.

Dose-response analyses of human data from the Iraqi epidemic of 1971 to 1972 have indicated correlations between maximal maternal hair levels during pregnancy and the severity of the neurological deficits seen in the children (Cox et al. 1989; Marsh et al. 1981, 1987). An evaluation of a calculated threshold for response is presented in Section 6.3.1 of this volume.

**Table 3-66**  
**Developmental Toxicity of Methylmercury in Humans: Case Studies**

Species/ No. per Sex	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Human/8 M, 7 F infants	~2 mo. (feed)	NS	Assessment of 15 mother-infant pairs where the mothers ate grain treated with methylmercury fungicide during pregnancy. Motor and mental development were impaired (blindness, impaired hearing) in 6 infants; there were no congenital malformations. BML: Affected infants: ~3,000 µg/L in blood at 2 months; Affected mothers: ≥400 µg/L in blood	Amin-Zaki et al. 1974
Human/1 F	6 mo. 3 mo. postcoital- term (feed)	NS	Severe neurological impairment (blindness, myoclonic seizures, spastic quadriplegia) of male infant born to a mother eating meat from pigs that had eaten grain treated with methylmercury fungicide. Limitation: Case report BML not reported	Snyder and Seelinger 1976

**Table 3-67**  
**Developmental Toxicity of Methylmercury in Humans: Epidemiologic Studies**

Species/ No. per Sex	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Human/220 F	NS (food)	NS	Mental retardation, atrophy of brain and degeneration of cerebellum in offspring. Of 220 infants born in Minamata (to mothers eating contaminated fish), 13 had severe symptoms; the number with less severe symptoms was not reported. Limitations: Few details on methods or results BML not reported	Harada 1978
Human/84 mother-child pairs	few days to several mo. (food)	NS	Assessment of mother-infant pairs where mothers ate grain treated with methylmercury fungicide during pregnancy (same Iraqi population as reported by Amin-Zaki et al. 1974). Severe psychomotor retardation in infants. BML Range: 37-293 µg/g in hair (maximum in segment of maternal hair)	Marsh et al. 1981
Human/243 exposed (sex NS) aged 12-30 mo.	Gestation and lactation (food)	NS	Abnormal tendon reflexes or muscle tone in male offspring correlated with methylmercury exposure ( $p < 0.05$ ). Conducted as a case-control study after potential affected measures were identified. Limitation: Author reported that the statistical method could have led to an association by chance. BML avg: 6 µg/g in maternal hair	McKeown-Eyssen et al. 1983
Human/81 mother-child pairs	few days to several mo. (food)	NS	Assessment of mother-infant pairs where mothers ate grain treated with methylmercury fungicide during pregnancy (same Iraqi population as reported by Amin-Zaki et al. 1974). Delayed walking and talking; seizures; mental retardation. BML Range: ~18-598 µg/g (maximum in strand) in hair of mothers of affected infants	Marsh et al. 1987

The developmental toxicity of oral exposure to methylmercury has been extensively studied in animals. In rodents exposed *in utero*, a spectrum of effects has been observed ranging from decreases in fetal weight and skeletal ossification and increases in skeletal variations and malformations (brain lesions, hydrocephalus, cleft palate, micrognathia, edema, subcutaneous bleeding, hydronephrosis, hypoplasia of the kidneys, dilation of the renal pelvis) to increased resorptions and fetal deaths (Fuyuta et al. 1978, 1979; Inouye and Kajiwara 1988a; Inouye and Murakami 1975; Khera and Tabacova 1973; Nolen et al. 1972; Reuhl et al. 1981; Yasuda et al. 1985). The severity of the effects generally increased with dose, and the incidence of malformations increased with exposures that occurred later in gestation (Fuyuta et al. 1978; Inouye and Murakami 1975). Brain lesions have been observed in a variety of areas including the brain mantle, corpus callosum, caudate putamen and cerebellum. In guinea pigs, early gestational exposures (weeks 3–5 of pregnancy) resulted primarily in developmental disturbances of the brain (smaller brains, dilated lateral ventricles and reduced size of caudate putamen), whereas later gestational exposures (>week 6 of pregnancy) resulted in widespread neuronal degeneration (Inouye and Kajiwara 1988b).

In addition to structural changes, functional changes have been observed in animals after gestational exposures. Such functional effects include abnormal tail position during walking; flexion;

hindlimb crossing; decreased locomotor activity, responding in an avoidance task and righting response; increased passiveness, startle-response and sensitivity to pentylenetetrazol-induced convulsions; and impaired maze performance, operant behavior, swimming behavior, tactile-kinesthetic function, visual recognition memory, temporal discrimination, and subtle learning deficits such as insensitivity to changing reinforcement contingencies (Bornhausen et al. 1980; Buelke-Sam et al. 1985; Burbacher et al. 1990; Elsner 1991; Geyer et al. 1985; Gunderson et al. 1988; Hughes and Annau 1976; Inouye et al. 1985; Musch et al. 1978; Olson and Boush 1975; Rice 1992; Rice and Gilbert 1990; Stoltenburg-Didinger and Markwort 1990; Suter and Schon 1986; Newland et al. 1994).

Overt neurological impairment is the endpoint used to document methylmercury poisonings; however, as shown in animal studies, methylmercury may produce more subtle neurodevelopmental effects such as impairment of sensory or cognitive systems. Schreiner et al. (1986) exposed rats to 0, 0.2 or 0.6 mg Hg/kg-day as methylmercuric chloride *in utero* and during lactation to evaluate pup performance on visual discrimination reversal task. While no overt signs of neurotoxicity were evident, subtle differences between the control and high-dose group were observed during more difficult tasks. A stressful or highly demanding situation appears to be necessary for the expression of these sensory effects, wherein the decreased ability to adapt to the altered conditions became manifest. Spyker et al. (1972) reported that although no signs of neurological toxicity was observed in mouse pups exposed to methylmercury *in utero*, open field and swimming tests revealed subtle neurological effects in the exposed pups. Newland et al. (1994) administered methylmercury by gavage to pregnant squirrel monkeys between weeks 11 and 14.5 of gestation. Doses were adjusted to maintain 0.7 to 0.9 ppm Hg in the maternal blood. There were three controls and three methylmercury-treated offspring. Offspring were evaluated at 5-6 on a lever pressing test which required discrimination between degrees of reinforcement. At steady state, monkeys exposed to methylmercury *in utero* were less sensitive to differences in reinforcement rates. When reinforcement rates changed, exposed animals either changed their behavior slowly in response to the altered reinforcement or not at all.

The developmental toxicity of methylmercury may be attributable to the ability of methylmercury to bind to sulfhydryl-rich tubulin (a protein component of microtubules) and cause its depolymerization (Falconer et al. 1994; Sager et al. 1983). Both cell division and cell migration require intact microtubules for normal functioning. Disruption of microtubule function could result in the derangement of cell migration (Choi et al. 1978; Falconer et al. 1994; Matsumoto et al. 1965) and arrested cell division (Reuhl et al. 1994; Sager et al. 1984).

**Table 3-68**  
**Developmental Toxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Rat/Charles River/20 F	9 d Gd 6-14 ad lib in drinking water	0, 0.02, 0.2, 4	Increased number of fetuses with soft tissue variations of the urinary system and incomplete ossification or calcification (LOAEL = 4; p<0.05). BML not reported	Nolen et al. 1972

**Table 3-68 (continued)**  
**Developmental Toxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Rat/Wistar/35 F	52 d ad lib in feed	0, 0.002, 0.01, 0.05, 0.25 (MMC)	Increased incidence of eye defects (in harderian and lachrymal glands) and salivary glands in fetuses (LOAEL = 0.25); significant dose response ( $p = 0.01$ ). Mothers were treated from immaturity through weaning or later. Limitations: Incomplete reporting; of results BML not reported	Khera and Tabacova 1973
Rat/Wistar/10 F	8, 12, or 20 d 1 x/d Gd 12-20, 0-12, or 0-20 (gavage)	2, 4 (MMC)	Increased brain lesions and generalized edema (Gd 0-20) (LOAEL = 2). Limitations: Limited data reporting; no statistical analysis; small number of treated animals BML not reported	Inouye and Murakami 1975
Rat/Holtzman/5 F	during gesta- tion, during lactation, or postnatal days 21-30 in drinking water	0, 2.5 (MMC)	Decreased visual evoked potential latencies for peaks N1 ( $p \leq 0.05$ ), P1 ( $p \leq 0.01$ ) and P2 ( $p \leq 0.01$ ) in 30-day old pups exposed during gestation, during lactation, or during postnatal days 21-30. BML not reported	Zenick 1976
Rat/Charles River CD/20 F	47 d prior to and during gestation ad lib in drinking water	0.42, 0.7, 1.4 (MMH)	Ultrastructural changes, dose-related decrease in biochemical activity in mitochondria of fetal hepatocytes ( $p < 0.01$ ) following administration of methylmercury hydroxide to mothers (LOAEL = 1.4). BML: 40 $\mu\text{g/g}$ (organic and inorganic) in liver of fetuses at 1.4 mg/kg-day	Fowler and Woods 1977
Rat/Long- Evans/4 exposed, 6 control	Once Gd 7 (gavage)	0, 4 (MMC)	Increased P1-N1 amplitudes and decreased P2 and N2 latencies of cortically visual evoked potential ( $p < 0.05$ ). BML not reported	Dyer et al. 1978
Rat/Wistar/20 F	8 d 1 x/d Gd 7-14 (gavage)	0, 2, 4, 6 (MMC)	At 6 mg/kg-day, decreased maternal weight gain, increased resorptions and fetal deaths ( $p < 0.001$ ); decreased fetal body weight increased skeletal and visceral malformations (hydrocephaly, wavy ribs). (LOAEL = 4; $p < 0.01$ ) BML not reported	Fuyuta et al. 1978
Rat/Wistar- Neuherberg/ No. F. NS	4 d Gd 6-9 (gavage)	0, 0.04, 1.6 (MMC)	Impaired ability to perform operant conditioning procedures (number of responses on lever required in specified period of time) (LOAEL = 0.05). Limitation: Statistical analyses not reported BML not reported	Musch et al. 1978
Rat/Wistar/10 F	4 d 1 x/d Gd 6-9 (gavage)	0, 0.004, 0.008, 0.035 (MMC)	Reduction in behavioral performance in offspring of treated mice following operant conditioning (LOAEL = 0.008; $p < 0.01$ ). BML not reported	Bornhausen et al. 1980

**Table 3-68 (continued)**  
**Developmental Toxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Rat/Sprague- Dawley/No. F NS	Once Gd 8 (gavage)	0, 6.3 (MMC)	Shorter avoidance latency in 60-day old offspring (LOAEL = 6.3). BML not reported	Cuomo et al. 1984
Rat/Sprague- Dawley/No. F NS	10 d 1 x/d Gd 6-15 (gavage)	0, 0.2, 1, 2, 4 (MMC)	Delayed sexual development (vaginal patency and testes descent), reduced pivoting, delayed surface righting, partially retarded swimming development, increased activity in center of open field, impaired startle reflex response. Reduced maternal weight gain and litter weight. No live offspring were produced at 4 mg/kg-day (LOAEL = 2; $p < 0.05$ ). BML not reported	Geyer et al. 1985
Rat/Sprague- Dawley/ 15-19 F	4 d 1 x/d Gd 6-9 (gavage)	0, 1.6, 4.8 (MMC)	Delayed vaginal patency, delayed surface righting, retarded swimming development, lower activity, impaired complex water maze performance. Increased mortality of pups at 1-21 days of age (LOAEL = 4.8; $p < 0.05$ ). BML not reported	Vorhees 1985
Rat/Wistar/ 38 M, 38 F	during gestation and lactation ad lib in drinking water	0, 0.2, 0.6 (MMC)	Increase in response latency in male ( $p < 0.05$ ) and female pups ( $p < 0.01$ ) and in passiveness ( $p < 0.05$ ) in visual discrimination reversal task at 0.6 mg/kg-day (LOAEL = 0.6). BML not reported	Schreiner et al. 1986
Rat/HAN- Wistar/10 F	13 days prior to mating until post- natal day 21 in drinking water	0, 0.2, 0.6, 1.7 (MMC)	Reduced weight gain, ataxia and inability to give birth in dams at 1.7. High mortality in pups at 1.7. Impaired swimming behavior and righting reflex, delayed sexual maturity (vaginal opening and testes descent) at 0.2 and 0.6. (LOAEL = 0.2; $p \leq 0.05$ ). BML = 9,700-191,000 $\mu\text{g/L}$ in dams and 10,000-127,000 $\mu\text{g/L}$ in pups at birth	Suter and Schon 1986
Rat/Wistar/No. F NS	4 d 1 x/d Gd 6-9 (gavage)	0, 0.02, 0.04, 0.4, 4 (MMC)	Increased startle response; impaired swimming behavior, decreased locomotor and nose-poking behavior; alteration of dendritic spine morphology (LOAEL = 4). Limitations: Limited data reporting; no statistical analysis BML not reported	Stoltenburg- Didinger and Markwort 1990
Rat/Wistar/16 F	2 wk prior to mating through weaning ad lib in drinking water	0, 0.08-0.38, 0.34-0.95 (MMC)	Impaired tactile-kinesthetic function ( $p \leq 0.05$ ) (LOAEL = 0.08-0.38). BML not reported	Elsner 1991



**Table 3-68 (continued)**  
**Developmental Toxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Rat/Sprague- Dawley/No. and sex NS	Once Gd 15 (gavage)	0, 6.4 (MMC)	Increased GABA <sub>A</sub> receptors in prenatally exposed pups sacrificed at 14 or 21 days postpartum; increased behavioral depression after diazepam. Limitations: Only one treatment level; no data on number of animals BML not reported	Guidetti et al. 1992
Mouse/SvSl/ No. F NS	Once Gd 7 or 9 (i.p.)	0, 0.16 mg MMD/20 g	Impaired swimming ability and open-field behavior ( $p<0.05$ ) in 30-day old pups. Dose administered as methylmercury dicyandiamide (MMD) BML not reported	Spyker et al. 1972
Mouse/CFW/No. F NS	Once Gd 8 (i.v.)	0, 1, 2, 3, 5, 10 (MMH)	Increased number of trials to criterion ( $p<0.05$ ) and increased number that failed to attain criterion in 2-way avoidance test conducted on 56-day old pups (LOAEL = 3). BML not reported	Hughes and Annau 1976
Mouse/ 129/Svsl/ No. F NS	Once Gd 10 (s.c.)	0, 5, 7, 10	Longer center square latency at 10 (once) and 3.5 (3 d), decreased rearings and increased backings at 3.5; decreased locomotor activity at 7 and 10; postnatal growth retardation at 7 and 10 (LOAEL = 7; $p<0.05$ ). BML not reported	Su and Okita 1976
Mouse/C57BL/ 10 F	8 d 1 x/d Gd 6-13 (gavage)	0, 2, 4, 4.8, 6 (MMC)	Increased resorptions and fetal deaths at 4.8 and 6 ( $p<0.01$ ); increased malformations (cleft palate, fused vertebrae) at 2 and higher ( $p<0.05$ ); increased skeletal variations; decreased maternal weight gain at 4.8 mg/kg-day (LOAEL = 2). Limitation: small number of treated animals BML not reported	Fuyuta et al. 1978
Mouse/ DUB/ICR/8 F exposed, 7 F controls	Once Gd 12 (gavage)	0, 8	Arrest of brain cells during mitosis ( $p<0.01$ ). Limitations: Only one dose tested; small number of animals tested BML not reported	Rodier et al. 1984
Mouse/ C3H/HeN/10 F	Once Gd 13, 14, 15, 16, or 17 (gavage)	0, 16 (MMC)	Decreased neonatal survival and weight gain; impaired righting response; decreased locomotor activity; abnormal gait; crossing of hindlimbs; decreased brain weight in groups treated on Gd 13 or 14 ( $p<0.01$ ); dilated lateral ventricles; slightly simplified cerebellar pattern. Effects were seen in groups dosed on all days, but somewhat stronger in those treated on Gd 13 or 14. Limitations: Incomplete reporting of data; most parameters were not analyzed statistically; only one dose tested BML: ~20 µg/g in brain of fetuses	Inouye et al. 1985

**Table 3-68 (continued)**  
**Developmental Toxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Guinea pig/ Hartley/5-9 F	Once Gd 21, 28, 35, 42, or 49 (gavage)	9.4-15 7.5 mg/animal (wt 500-800 g) (MMC)	Aborted litters and retarded fetal brain development at all treatment times. Limitations: No statistical analysis; small number of treated animals, only 1 day of dosing Avg BML over treatment time: Fetal: 2,600 µ/L in blood; Maternal: 1,800 µg/g in blood	Inouye and Kajiwara 1988b
Hamster/ Golden/10 F	Once at Gd 10, or 6 d 1 x/d Gd 10-15 (gavage)	0, 1.6, 8 (MMC)	Degeneration of cerebellar neurons in rats born to mothers treated with 1.6 mg/kg/d on Gd 10-15 or a single dose of 8 mg/kg on Gd 10 and sacrificed neonatally or as adults. Limitation: small number of treated animals BML not reported	Reuhl et al. 1981
Monkey/ <i>Macaca fascicularis</i> /9 F exposed, 8 F control	approx. 1-3 yr 1 x/d prior to mating through gestation (in apple juice)	0, 0.04, 0.06	Impaired visual recognition memory (data pooled from both groups of infants of exposed mothers) compared to unexposed controls; test performed at 50-60 days of age. Limitation: small number of treatment animals BML Range: 880-2,450 µg/L in blood of infants at birth; 280-830 µg/L at testing	Gunderson et al. 1988
Monkey/ <i>Macaca fascicularis</i> /12 F exposed, 13 F control	approx. 4 mo to 2 yr 1 x/d prior to mating through gestation (in apple juice)	0, 0.04	Decrease in social play behavior and concomitant increase in nonsocial passive behavior compared to unexposed controls; tests performed at 2 weeks to 8 months of age. Limitation: small number of treatment animals BML Range: 1,565 µg/L in blood of infants at birth	Gunderson et al. 1988
Monkey/ <i>Macaca fascicularis</i> /5 mothers	4-4.5 yr 1 x/d in utero and postnatally (gavage)	0, 0.01, 0.025, 0.5 (MMC)	Spatial visual impairment (LOAEL = 0.01). Limitation: Small number of infants (5 high-dose; 2 mid-dose; 1 low-dose) BML not reported	Rice and Gilbert 1990
Monkey/ <i>Macaca fascicularis</i> /4 M, 1 F exposed, 1 M, 2 F controls	6.5-7 yr 7 d/wk 1 x/d (capsule; gavage)	0, 0.05 (MMC)	Six years after end of dosing (follow-up study to Rice and Gilbert 1982); decreased fine motor performance; diminished touch and pinprick sensitivity; impaired high frequency hearing ( $p < 0.05$ ). Limitations: small number of animals tested; one dose level tested BML: Not detectable at time of dosing	Rice 1989b; Rice and Gilbert 1992
Monkey/ <i>Macaca fascicularis</i> /13 total	4-4.5 yr 1 x/d in utero and postnatally (gavage)	0, 0.01, 0.025, or 0.05	Monkeys tested as juveniles showed no gross intellectual impairment; some indication of decreased temporal discrimination. BML in treated animals at birth averaged 0.46, 0.93, or 2.66 ppm; decreased to steady-state of 0.20, 0.25 or 0.60 ppm.	Rice 1992.

**Table 3-68 (continued)**  
**Developmental Toxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Monkey/ <i>Macaca fascicularis</i> /23 F	unspecified period prior to mating through gestation	0.04, 0.06, 0.08	No effect on spatial memory of adult offspring of animals treated with methylmercury hydroxide (data pooled from 24 animals, all treated groups). BML Range: 1,040-2,460 µg/L in blood of infants at birth	Gilbert et al. 1993
Monkey/ <i>Saimiri sciureus</i> /3 F	week 11 or 14.5 until parturition (gavage)	0.7 to 0.9 ppm methylmercury in maternal blood	Monkeys exposed <i>in utero</i> tested (on learned lever pulling activity) at ages 5-6 yr. Methylmercury treatment resulted in decreased sensitivity to degrees in reinforcement; change in reinforcement degree resulted in either no behavior change or slow change by comparison to controls. Limitations: small number of animals tested; incomplete reporting on treatment.	Newland et al. 1994

### 3.3.3.9 Reproductive

Although no data were located regarding the reproductive effects of oral exposure to methylmercury in humans, animal data suggest that, at sufficiently high doses, methylmercury may adversely affect reproductive function in both males and females. When male rats were given methylmercury for several days prior to mating, mated females were observed with increased preimplantation losses (Khera 1973). Exposure of male monkeys to methylmercury for longer durations has been shown to adversely affect sperm motility and speed and to result in increased incidences of sperm tail defects (Mohamed et al. 1987). Decreases in spermatogenesis and tubular atrophy of the testes have been observed upon histopathological analyses of the testes of mice exposed to methylmercury chronically (Hirano et al. 1986; Mitsumori et al. 1990).

Less information is available regarding the effects of methylmercury on female reproductive function. Exposure of female monkeys to methylmercury for 4 months prior to mating produced no effects on the length of the menstrual cycle but resulted in decreased conceptions and increased early abortions and stillbirths (Burbacher et al. 1988). Several studies have shown increased rates of resorptions and abortions after exposure during gestation (Fuyuta et al. 1978; Hughes and Annau 1976; Inouye and Kajiwara 1988a); however, it is unclear from these studies whether the effects observed are the result of maternal reproductive failure or fetal toxicity.

**Table 3-69**  
**Reproductive Toxicity of Methylmercury in Animals**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Rat/Wistar/10-20 M	7 d 1 x/d (gavage)	0, 1, 2.5, 5 (MMC)	Reduced mean litter size after male exposure (LOAEL = 5; p<0.01) in sequential mating trials with unexposed females BML not reported	Khera 1973
Rat/Wistar/14-19 M	95-125 d 1 x/d	0.1, 0.5, 1 (MMC)	Males were mated to unexposed females concurrent with dosing. Reduced mean litter size (LOAEL = 0.5) BML not reported	Khera 1973
Mouse/Swiss Webster/10-20 M	5-7 d 1 x/d (gavage)	0, 1, 2.5, 5 (MMC)	No effect on number of viable embryos, dead embryos, or percent pregnancy (NOAEL = 5) BML not reported	Khera 1973
Mouse/ICR/60 M, 60 F	104 wk ad lib in feed	0, 0.03, 0.15, 0.72 (M); 0.02, 0.11, 0.62 (F) (MMC)	Significantly decreased spermatogenesis (LOAEL = 0.73; significance level not reported) BML not reported	Hirano et al. 1986
Mouse/B6C3F <sub>1</sub> /60 M, 60 F	104 wk ad lib in feed	0, 0.03, 0.14, 0.68 (M); 0.03, 0.13, 0.6 (F) (MMC)	Tubular atrophy of the testes (LOAEL = 0.69; p<0.01) BML not reported	Mitsumori et al. 1990
Monkey/ <i>Macaca fascicularis</i> /3 M	20 wk 7 d/wk 1 x/d (gavage)	0, 0.047, 0.065	Decreased sperm motility and speed; increased sperm tail defects (LOAEL = 0.065; p<0.05) BML: ~2200 µg/L in blood at 0.065 mg/kg-day, approaching steady state	Mohamed et al. 1987
Monkey/ <i>Macaca fascicularis</i> /7-9 F	4 mo prior to mating 1 x/d (gavage)	0, 0.04, 0.06, 0.08 (MMH)	Abortion; stillbirth; decreased conception in exposed females (LOAEL = 0.06); no effect on menstrual cyclicity Avg. BML: 1,600 µg/L in blood at equilibrium at 0.06 mg/kg	Burbacher et al. 1988

### 3.3.3.10 Genotoxicity

Data from several studies in humans suggest that ingesting methylmercury may cause chromosomal aberrations and sister chromatid exchange (Skerfving et al. 1970, 1974; Wulf et al. 1986; Franchi et al. 1994).

A study of nine Swedish subjects who consumed mercury-contaminated fish and 4 controls showed a statistically significant rank correlation between blood mercury and percentage of lymphocytes with chromosome breaks (Skerfving et al. 1970). An extension of this study (Skerfving et al. 1974) included 23 "exposed" (5 females and 18 males) and 16 "controls" (3 females and 13 males). The authors

reported a significant correlation between blood mercury level and frequency of chromatid changes and "unstable" chromosome aberrations; there was no correlation with "stable" chromosome aberrations.

The Wulf et al. (1988) study was of 92 Greenland Eskimos. Subjects were divided into three groups based on intake of seal meat (6 times/week; 2-5 times/week; once/week or no consumption of seal meat). Higher frequency of SCE in lymphocytes was correlated with blood mercury concentration; an increase of 10 µg Hg/L in blood was associated with an increase of 0.3 SCE/cell. Positive correlations were also found for smoking, diet, living district and cadmium exposure.

Franchi et al. (1994) evaluated formation of micronuclei in peripheral blood lymphocytes of Mediterranean fishers, a group with presumed high exposure to methylmercury. Fifty-one subjects were interviewed on age, number of seafood-based meals/week and habits such as smoking and alcohol consumption. Total blood mercury was measured; the range was 10.08 – 304.11 ng/g with a mean of  $88.97 \pm 54.09$  ng/g. There was a statistically significant correlation between blood mercury concentration and micronucleus frequency and between age and micronucleus frequency.

**Table 3-70**  
**Genotoxicity of Methylmercury in Humans: Case Study**

Species/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Human/6 M, 3 F exposed; 3 M, 1 F control	>5 yr ≥ 3 x/wk	NS	Correlation between blood mercury concentration and chromosome breaks in lymphocytes cultured from people who ate mercury-contaminated fish Limitation: Small sample size; limited exposure data BML Range: 4-650 µg/L in blood	Skerfving et al. 1970

**Table 3-71**  
**Genotoxicity of Methylmercury in Humans: Epidemiology Study**

Species/ No. per Sex	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Human/24-63 (both sexes)	NS	NS	Incidence of sister chromatid exchanges (SCEs) in cultured peripheral lymphocytes correlated with intake of seal meat in an Eskimo population (as a surrogate for mercury intake); $p = 0.001$ . Other factors also correlated with SCEs, but multiple regression analysis found that some of the effect was attributable to mercury. Limitation: Limited exposure data BML not reported	Wulf et al. 1986

**Table 3-71 (continued)**  
**Genotoxicity of Methylmercury in Humans: Epidemiology Study**

Species/ No. per Sex	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Human / 51 M	measured as seafood meals/ week. Range 2 - 14.	NS	Incidence of micronuclei positively correlated with blood mercury concentration and with age. No correlation with smoking or number of seafood meals /week. Limitation: no control group. BML range: 10.08 - 403.11 µg/g blood.	Franchi et al. 1994.
Human/18M exposed/10 control	10.5 yr (occup)	0.15-0.44 (HgCl <sub>2</sub> )	Increased frequency of chromosomal breaks. Limitations: Workers also exposed to mercuric chloride and one worker had history of benzene poisoning; control group was not matched for sex, smoking habits, or sample size. BML: ≈890 µg/L in urine (avg)	Popescu et al. 1979

In a study with cats (Charbonneau et al. 1976), methylmercury did not induce dose-related unscheduled DNA synthesis in lymphocytes or chromosomal aberrations in bone marrow cells after oral exposure to methylmercury for up to 39 months (Miller et al. 1979). Statistically significant decreases in unscheduled DNA synthesis and increases in chromosomal aberrations were observed, but there was no dose-response.

**Table 3-72**  
**Genotoxicity of Methylmercury in Cats**

Species/ Strain/ No. per Sex per Group	Exposure Duration	Dose (mg/kg-day)	Effects/Limitations/BML	Reference
Cat/Breed and sex NS	39 mo 7 d/wk	0.008, 0.020, 0.046	No dose-related changes in unscheduled DNA synthesis in cultured lymphocytes or frequency of chromosomal aberrations in bone marrow of cats fed mercury-contaminated fish or a fish diet supplemented with methylmercuric chloride Limitations: No positive control; no assessment of cytotoxicity BML Range: 500-13,500 µg/L Hg in blood	Miller et al. 1979

Strain-specific differences exist with respect to the ability of methylmercury to produce dominant lethal effects in mice (Suter 1975). When (SEC x C<sub>57</sub>Bl)F<sub>1</sub> males were injected with 10 mg/kg methylmercury hydroxide, there was a slight reduction in the total number of implantations and a decrease in the number of viable embryos. This was not observed when (101 x C<sub>3</sub>H)F<sub>1</sub> males were

exposed in a similar fashion. When female (10 x C<sub>3</sub>H)F<sub>1</sub> mice were treated with methylmercuric hydroxide, no increase in the incidence of dead implants was observed (unlike the case for mercuric chloride). Changes in chromosome number but no increase in chromosome aberrations were observed in oocytes of Syrian hamsters treated with one i.p injection of 10 mg/kg methylmercuric chloride (Mailhes 1983). Methylmercury was administered s.c. to golden hamsters at doses of 6.4 mg or 12.8 mg Hg/kg/body weight. Polyploidy and chromosomal aberrations were increased in bone marrow cells, but there was no effect on metaphase II oocytes. There was an inhibitory effect on ovulation which the authors noted was not as severe as that induced by mercuric chloride in the same study (Watanabe et al. 1982). Non-dysjunction and sex-linked recessive lethal mutations were seen in *Drosophila melanogaster* treated with methylmercury in the diet (Ramel 1972).

As reviewed in WHO (1990), methylmercury is not a potent mutagen but is capable of causing chromosome damage in a variety of systems. *In vitro* studies have generally shown clastogenic activity but only weak mutagenic activity. Methylmercuric chloride and dimethylmercury were both shown to induce chromosome aberrations and aneuploidy in primary cultures of human lymphocytes; methylmercuric chloride was the more potent clastogen at equally toxic doses (Betti et al. 1992). Both methylmercury and mercuric chloride induced a dose dependent increase in SCE in primary human lymphocytes and muntjac fibroblasts; methylmercury was about five time more effective in this regard (Verschaeve et al. 1984; Morimoto et al. 1982).

Methylmercury has been shown to inhibit nucleolus organizing activity in human lymphocytes (Verschaeve et al. 1983). Methylmercury can induce histone protein perturbations and has been reported to interfere with gene expression in cultures of glioma cells (WHO 1990). Impaired growth and development was noted in cultured mouse embryonic tissue treated *in vitro* with methylmercuric chloride, but there was no increase in SCE (Matsumoto and Spindle 1982). Costa et al. (1991) showed that methylmercuric chloride caused DNA strand breaks in both V79 and rat glioblastoma cells treated *in vitro*. Methylmercuric chloride produced more strand breaks than did mercuric chloride.

Evidence of DNA damage has been observed in the *Bacillus subtilis* rec-assay (Kanematsu et al. 1980). These authors reported negative results for methylmercury in spot tests for mutagenicity in the following bacterial strains: *E. coli* B/r WP2 and WP2; and *Salmonella typhimurium* strains TA1535, TA1537, TA1538, TA98 and TA100. Jenssen and Ramel (1980) in a review article indicated that methylmercury acetate was negative in both micronucleus assays and in mutagenicity tests in *Salmonella*; the article referred to Heddle, J.R. and W.R. Bruce (1977) and provided no experimental details. Weak mutagenic responses for methylmercuric chloride and methoxyethyl mercury chloride were observed in Chinese hamster V79 cells at doses near the cytotoxic threshold (Fiskesjo 1979), and methylmercury produced a slight increase in the frequency of chromosomal nondisjunction in *Saccharomyces cerevisiae* (Nakai and Machida 1973). Methylmercury, however, caused neither gene mutations nor recombination in *S. cerevisiae* (Nakai and Machida 1973). Methylmercury retarded DNA synthesis and produced single strand breaks in DNA in L5178Y cells (Nakazawa et al. 1975).

## 4. SUSCEPTIBLE POPULATIONS

A susceptible population is a group who may experience more severe adverse effects at comparable levels or adverse effects at lower exposure levels than the general population. The greater response of these sensitive subpopulations may be a result of a variety of intrinsic or extrinsic factors. Volume V describes populations that may be at increase risk because of higher exposure to mercury and mercury compounds. Additional factors that may be important include, but are not limited to, the following: an impaired ability of the detoxification, excretory, or compensatory processes in the body to protect against or reduce toxicity; differences in physiological protective mechanisms (e.g., blood brain barrier); or unique toxic reactions that are specific to the genetic makeup, developmental stage, health status, gender or age of the individual.

The nervous and renal systems are the primary targets for mercury-induced toxicity. Data are also available indicating some effects to the respiratory, cardiovascular, gastrointestinal, hematologic, immune, and reproductive systems. The developing organism appears to be particularly sensitive to methylmercury exposure. In addition, it is probable that individuals with preexisting damage or disease in target organs for mercury-induced toxicity may experience more severe effects upon exposure to mercury. The populations listed below may be highly susceptible to mercury toxicity.

- Developing Organisms. Data from epidemic poisonings in Japan (Harada 1978) and Iraq (Marsh et al. 1987) indicate that infants exposed *in utero* to methylmercury developed marked neurological development delays while their mothers experienced little or no overt signs of toxicity. Data indicate that the developing fetus may be 5 to 10 times more sensitive than the adult (Clarkson, 1992). This difference in sensitivity is believed to be due, in part, to the high sensitivity of developmental processes (i.e., cellular division, differentiation, and migration) to disruption by mercury (Choi et al. 1978; Sager et al. 1982). One factor that may account for this difference in sensitivity is the presence of an incomplete blood brain barrier in the fetus. Another important factor may be the lack of methylmercury excretion in the fetus (Grandjean et al. 1994).
- Age - Infants and Other Age Groups. Available data indicate that neonates are at increased risk to inorganic mercury and methylmercury. Both inorganic and organic forms of mercury are excreted in breast milk (Sundberg and Oskarsson 1992; Yoshida et al. 1992; Grandjean et al. 1994); thus, neonates in an exposed population may experience increased mercury exposure. Animal data for rats indicate that suckling infants retain a higher percentage of ingested inorganic mercury than do adults (Kostial et al. 1978). The most significant difference in organ retention (neonates > adults) was methylmercury in the brain following exposure to methylmercury (Yang et al. 1973; Kostial et al. 1978) and inorganic mercury retained in the kidney following exposure to elemental mercury (Yoshida et al. 1992). These differences may be associated with an increased absorption of mercury with a milk diet, a decrease in excretion, or an incomplete blood brain barrier (Kostial et al. 1978, Grandjean et al. 1994).

Signs of toxicity may begin to be manifested several years after the cessation of dosing, possibly related to subclinical effects being unmasked by aging. Rice (1989b) dosed monkeys with methylmercury from birth to 6.5-7 years of age. Although there were no overt signs of neurotoxicity during dosing, neurological deficits were observed at 13



years of age, 6-7 years following cessation of exposure. Similarly, a small human population with Minamata disease has been identified in Japan as experiencing new or worsening neurological effects a few years following termination of mercury exposure. This late-onset Minamata disease may be related to several factors including aging (Igata 1993).

- Gender. Sex-related differences in mercury toxicokinetics and sensitivity to mercury have been observed, although data indicate that the more sensitive sex may differ by species and strain. Using death as the critical endpoint, in one strain of mice, C57BL/6N, males were less sensitive to methylmercury following daily dosing than females while, in contrast, male mice were more sensitive than females in another strain, BALB/cA (Yasutake and Hirayama 1988). In humans, although the ratio of males to females with Minamata disease has been reported to be 1.2:1, the ratio of deaths was recorded at 1.8:1 (Tamashiro et al. 1984).

Other studies are in general agreement that male rats (Thomas et al. 1986) and mice (Nielsen and Andersen 1991a, 1991b) eliminate mercury faster and have lower tissue levels than females following dosing with methylmercury. Part of the difference in whole-body retention of mercury in methylmercury-exposed mice has been associated with varying degrees of deposition of mercury in the carcass, including the skin and hair (Nielsen and Andersen 1991b). This difference is thought to be due in part to differences in glutathione metabolism and renal excretion of mercury, which is affected by the hormonal status of testosterone (Nielsen et al. 1994). Hirayama et al. (1987) have reported that the toxicokinetics of methylmercury in castrated male mice was very similar to that in female mice, and that the male pattern of methylmercury toxicokinetics could be restored by testosterone treatment. Such differences were not observed in a small set of similarly tested human volunteers (Miettinen et al. 1971).

- Dietary Insufficiencies of Zinc, Glutathione, or Antioxidants. Mercury has been suggested to cause tissue damage by increasing the formation of reactive oxygen species and activation of lipoperoxidation, calcium-dependent proteolysis, endonuclease activity, and phospholipid hydrolysis (Ali et al. 1992; LeBel et al. 1990, 1992; Gstraunthaler et al. 1983; Verity and Sarafian 1991). Zinc, glutathione, and antioxidant deficiencies would be expected to exacerbate mercury-induced damage by limiting cellular defenses against the oxidative processes. Animal data support the importance of zinc, glutathione, and antioxidants in limiting mercury-induced damage (Fukino et al. 1992; Girardi and Elias 1991; Yamini and Sleight 1984) (see also Section 5, Interactions).
- Predisposition for Autoimmune Glomerulonephritis. Autoimmune glomerulonephritis is a form of renal toxicity characterized by proteinuria, deposition of immune material (i.e., autoantibodies and complement C3) in the renal mesangium and glomerular blood vessels and glomerular cell hyperplasia (Bigazzi 1992; Goldman et al. 1991; Mathieson 1992). Limited human data suggest that certain individuals may develop this autoimmune response when exposed to inorganic or elemental mercury (Cardenas et al. 1993; Langworth et al. 1992b; Tubbs et al. 1982). While the etiology of this syndrome has not been completely elucidated, data from susceptible and resistant strains of animals indicate that susceptibility is governed by both major histocompatibility complex (MHC)

## 6.4 Risk Assessments Done By Other Groups

Quantitative estimates of hazards of oral exposure to methylmercury exposure have been considered by the Food and Drug Administration, Agency for Toxic Substances and Disease Registry (ATSDR), the Department of Energy and several State agencies. Several inhalation workplace exposure limits are available in the United States and other countries.

### 6.4.1 Food and Drug Administration

In 1969, in response to the poisonings in Minamata Bay and Niigata, Japan, the U.S. FDA proposed an administrative guideline of 0.5 ppm for mercury in fish and shellfish moving in interstate commerce. This limit was converted to an action level in 1974 (Federal Register 39, 42738, December 6, 1974) and increased to 1.0 ppm in 1979 (Federal Register 44, 3990, January 19, 1979) in recognition that exposure to mercury was less than originally considered. In 1984, the 1.0 ppm action level was converted from a mercury standard to one based on methylmercury (Federal Register 49, November 19, 1984).

The action level takes into consideration the tolerable daily intake (TDI) for methylmercury, as well as information on seafood consumption and associated exposure to methylmercury. The TDI is the amount of methylmercury that can be consumed daily over a long period of time with a reasonable certainty of no harm. U.S. FDA (and WHO) established a TDI based on a weekly tolerance of 0.3 mg of total mercury per person, of which no more than 0.2 mg should be present as methylmercury. These amounts are equivalent to 5 and 3.3  $\mu\text{g}$ , respectively, per kilogram of body weight. Using the values of methylmercury, this tolerable level would correspond to approximately 230  $\mu\text{g}/\text{week}$  for a 70 kg person or 33  $\mu\text{g}/\text{person}/\text{day}$ . The TDI was calculated from data developed in part by Swedish studies of Japanese individuals poisoned in the episode of Niigata which resulted from the consumption of contaminated fish and shellfish and the consideration of other studies of fish-eating populations.

Based on observations from the poisoning event later in Iraq, U.S. FDA has acknowledged that the fetus may be more sensitive than adults to the effects of mercury (Federal Register 44: 3990, January 19, 1979; Cordle and Tollefson, 1984, U.S. FDA Consumer, September, 1994). In recognition of these concerns, U.S. FDA has provided advice to pregnant women and women of child-bearing age to limit their consumption of fish known to have high levels of mercury (U.S. FDA Consumer, 1994). U.S. FDA believes, however, that given existing patterns of fish consumption, few women (less than 1%) eating such high mercury fish will experience slight reductions in the margin of safety. However, due to the uncertainties associated with the Iraqi study, U.S. FDA has chosen not to use the Iraqi study as a basis for revising its action level. Instead, the U.S. FDA has chosen to wait for findings of prospective studies of fish-eating populations in the Seychelles Islands and in the Faroes Islands.

#### 6.4.2 ATSDR

ATSDR has established Minimal Risk Levels (MRLs) for elemental, inorganic and methylmercury (ATSDR 1994). Recently a revised Toxicological Profile has been released for public comment (ATSDR 1997).

An acute inhalation MRL of  $0.00002 \text{ mg/m}^3$  has been derived for elemental mercury vapor based on neurodevelopmental changes in rats. Specifically, the effects were changes in locomotor activity at 4 months of age and an increased time to complete a radial arm maze at 6 months of age following exposure to  $0.05 \text{ mg Hg/m}^3$  for 1 hour during post-partum days 11–17 (Fredriksson et al. 1992). A chronic inhalation MRL of  $0.000014 \text{ mg/m}^3$  was derived for elemental mercury vapor based on a significant increase in the average velocity of naturally occurring tremors in occupational workers (Fawer et al. 1983). The revised chronic MRL is calculated to be  $0.0002 \text{ mg/m}^3$  by application of an uncertainty factor of 30 to a LOAEL of  $0.026 \text{ mg/m}^3$  for increased frequency of tremors in occupationally exposed workers (Fawer et al. 1983).

Acute and intermediate oral MRLs were derived for inorganic mercury based on kidney effects reported in the 1993 NTP study of mercuric chloride. The acute oral MRL was  $0.007 \text{ mg Hg/kg-day}$  based on a 2-week study reporting a NOAEL of  $0.93 \text{ mg Hg/kg-day}$  for renal effects in rats (NTP 1993). At higher doses, an increased incidence of tubular necrosis was observed. The intermediate oral MRL of  $0.002 \text{ mg Hg/kg-day}$  was established, based on a 6-month study reporting a NOAEL of  $0.23 \text{ mg Hg/kg-day}$  for renal effects (increased absolute and relative kidney weights) (NTP 1993). There is no indication that these values have been revised in the 1997 document.

An acute-intermediate oral MRL of  $0.00012 \text{ mg Hg/kg-day}$  was established in 1994 for methylmercury. ATSDR derived their assessment from the Marsh et al. (1981) and Cox et al. (1989) data; the MRL is based on the lowest observed peak of total mercury concentration in maternal hair ( $0.0012 \text{ mg/kg-day}$  equivalent to a LOAEL of 14 ppm mercury in maternal hair) during pregnancy associated with a delayed onset of walking in offspring in Iraqi children. This assessment is discussed in section 6.3.1.1 of this volume.

The 1997 Toxicological Profile calculates a chronic MRL for methylmercury of  $0.5 \text{ } \mu\text{g/kg/day}$ . This report chooses as a NOAEL the median maternal hair mercury of 5.9 ppm reported by Davidson et al. (1995) for the 29 month old Seychellois children tested with the BSID and Bayley Infant Behavior record. The Toxicological Profile characterizes the reported decrease in the male children's activity level as not adverse and chooses use of a midpoint of all measured maternal hair levels rather than the highest measure or median of the top quartile. Dose conversion was done as in the 1994 document to give an estimated ingested dose of  $0.5 \text{ } \mu\text{g/kg/day}$ . An uncertainty factor was not used to account for human variability.

#### 6.4.3 Department of Energy

Brookhaven Laboratories has prepared a report for Office of Clean Coal Technology, DOE. This report describes a probabilistic-based assessment which considered the potential increased health risk for paresthesia in adults. Their estimate is based upon a yearly emission rate of 180 kg/year from all fossil fuel power plants in the United States. This estimate represents less than 1% of the existing global pool of mercury that is introduced into the environment. Based upon the most sensitive adult sign of paresthesia, the mercury emissions from power plants would result in an increased risk for paresthesia of 0.004–0.007% with an upper 95th percentile risk of 0.013–0.017% (Lipfert et al. 1994).

#### 6.4.4 National Institute of Environmental Health Sciences (NIEHS)

NIEHS, part of the National Institutes of Health, was required under section 301 of the CAA "to conduct, and transmit to the Congress by November 15, 1993, a study to determine the threshold level of mercury exposure below which adverse human health effects are not expected to occur." In section 112 (n)(1)(C), NIEHS was encouraged to evaluate the health effects threshold for mercury in the absence of specifics as to species of mercury but to consider mercury in fish. As mercury in fish is primarily in the form of methylmercury, the NIEHS limited their consideration to this species.

The report was completed in 1993 and delivered to Office of Management and Budget for clearance. It describes dose- response assessments for methylmercury done by WHO, FDA and U.S. EPA and presents all three estimates as recommended for tolerable mercury concentrations. The NIEHS report also describes estimates of fish consumption by the U.S. population.

#### 6.4.5 Department of Labor

OSHA established a Permissible Exposure Limit (PEL), time-weighted average of 0.05 mg Hg/m<sup>3</sup> for mercury vapor, with a notation for skin exposure (U.S. Department of Labor 1989). A PEL as a ceiling value of 0.1 mg Hg/m<sup>3</sup>, also with a notation for dermal exposure was set for aryl mercury and inorganic mercury compounds.

NIOSH determined a Recommended Exposure Limit (REL), time-weighted average, of 0.05 mg Hg/m<sup>3</sup> for mercury and 0.1 mg Hg/m<sup>3</sup> for aryl and inorganic mercury compounds (NIOSH 1973, 1988).

#### 6.4.6 Various States

A number of states have released fish consumption advisories based upon their independent analysis of the available scientific literature for methylmercury. Most active among these states are Michigan, New Jersey, Maine, Idaho, and Oregon. Generally, there is a trend to move to more conservative values based upon developmental neurotoxicity defined in the Marsh et al. (1981) and Cox et al. (1989) papers. The methylmercury RfD of  $0.7 \times 10^{-4}$  mg/kg-day used by the state of New Jersey is discussed in section 6.3.1.1. Some states are waiting for more specific guidance from U.S. EPA.

#### 6.4.7 World Health Organization

The International Programme on Chemical Safety (IPCS) of the World Health Organization published a criteria document on mercury (WHO 1990). In that document, it was stated that "a daily intake of 3 to 7 µg Hg/kg body weight would cause adverse effects of the nervous system, manifested as an approximately 5% increase in the incidence of paraesthesias". The IPCS expert group also concluded that developmental effects in offspring (motor retardation or signs of CNS toxicity) could be detected as increases over background incidence at maternal hair levels of 10–20 ppm mercury. These levels of concern were based on evaluation of data including the human poisoning incident in Iraq described in Chapter 3.

#### 6.4.8 ACGIH

The ACGIH has established Threshold Limit values (TLV) as eight-hour time-weighted averages. They include the following:

Aryl mercury compounds	0.1 mg Hg/m <sup>3</sup>
Mercury vapor	0.05 mg Hg/m <sup>3</sup>
Inorganic mercury	0.1 mg Hg/m <sup>3</sup>

No STEL is recommended at this time. The Biological Exposure Indices Committee has recommended values for inorganic mercury in urine and blood of 35 µg/g creatinine and 15 µg/L respectively.

The ACGIH classified inorganic mercury including elemental mercury as follows: A4- Not classifiable as a Human Carcinogen: There are inadequate data on which to classify the agent in terms of its carcinogenicity in humans and/or animals.

## 7. ONGOING RESEARCH AND RESEARCH NEEDS

### 7.1 Ongoing Research

Table 7-1 lists ongoing research projects abstracted from the Federal Research in Progress Data Base (FEDRIP, 1994).

**Table 7-1  
Ongoing Research**

Investigator	Affiliation	Research Description	Sponsor
<i>Human</i>			
T. Clarkson	University of Rochester, Rochester, NY	Dose-response relationships in humans exposed to methylmercury and prenatal and early postnatal body burdens of methylmercury.	National Institute of Environmental Health Sciences (NIEHS)
P. Grandjean	Odense University, Odense, Denmark	Neurotoxicity risk from exposure to methylmercury from seafood	NIEHS
W. Markesbery	University of Kentucky, Lexington, KY	Role of mercury and dental amalgams in Alzheimer's disease	National Institute on Aging
M. Martin	University of Washington, Seattle, WA	Epidemiology of mercury in dentists	National Institute of Dental Research
R. Mitchell	University of Kentucky, Lexington, KY	Amalgam restorations and the relative risk of adverse pregnancy outcome	National Institute of Dental Research
G. Myers	University of Rochester, Rochester, NY	Child development following prenatal methylmercury exposure via fish	NIEHS
T. Okabe	Baylor College of Dentistry, Dallas, TX	Establish maximum levels of exposure from amalgams for dental patients and personnel	National Institute of Dental Research
M. Owens	Science Applications International Corp, Falls Church, VA	Potential and adverse effects associated with dental amalgam	National Institute of Dental Research
M. Rosenman	Morehouse College, Atlanta, GA	Effect of mercury in amalgam and urine to cognitive functioning in children	National Institute of General Medical Sciences
D. Savitz	University of North Carolina Chapel Hill, Chapel Hill, NC	Mercury and reproductive health in women dentists	National Institute of Dental Research
<i>Animal</i>			
P. Bigazzi	University of Connecticut, Farmington, CT	Mercury induced auto-immune disease in rats	NIEHS
T. Burbacher	University of Washington, Seattle, WA	Developmental effects of methylmercury in monkeys and rats	NIEHS
K. Mottet	University of Washington, Seattle, WA	Long-term toxicity associated with inorganic mercury and methylmercury	NIEHS
K. Pollard	University of California, San Diego, CA	Animal model of systemic autoimmunity induced by mercury	National Institute of Arthritis and Musculoskeletal and Skin Diseases

**Table 7-1**  
**Ongoing Research (continued)**

Investigator	Affiliation	Research Description	Sponsor
B. Weiss	University of Rochester, Rochester, NY	Neurotoxicity throughout the lifespan of mice exposed prenatally to methylmercury	NIEHS
<i>Mechanistic</i>			
W. Atchison	Michigan State University, East Lansing, MI	Neurotoxic mechanism of chronic methylmercury poisoning	NIEHS
D. Barfuss	Georgia State University, Atlanta, GA	Transport and toxicity of inorganic mercury in the nephron	NIEHS
T. Jensen	Herbert H. Lehman College, New York, NY	Effect on membrane structure and organelle distribution	National Institute of General Medical Sciences
D. Lawrence	Albany Medical College, Albany, NY	Effects of metals on the structure and function of murine and human lymphocytes	NIEHS
R. Noelle	Dartmouth Medical School, Hanover, NH	Effect of mercury on $\beta$ -lymphocyte function	NIEHS
K. Pollard	Scripps Research Institute, San Diego, CA	Mechanisms of autoantibody response induced by mercury which target the nucleolus	National Institute of Allergy and Infectious Diseases
B. Rajanna	Selma University, Selma, AL	Biomechanisms of heavy metal toxicity in rats	National Institute of General Medical Sciences
K. Ruehl	Rutgers University, New Brunswick, NJ	Mechanism of methylmercury neurotoxicity during development in mice	NIEHS
T. Sarafian	University of California, Los Angeles, CA	Effect of methylmercury on protein phosphorylation in cerebellar granule cells in brain	NIEHS
J. Stokes	Mount Desert Island Biological Lab, Salsbury Cove, ME	Effects of mercurials on transport properties of the bladder	NIEHS
R. Zalups	Mercer University School of Medicine	Cytotoxicity of mercuric chloride to isolated rat proximal tubular cells	NIEHS

Two of these ongoing studies deserve further discussion because they may fill critical data needs for the development of a reference dose for methylmercury. The first is the Seychelles Islands Study led by Dr. T.W. Clarkson from the University of Rochester. The objective of this study is to define the extent of human health risks from prenatal exposure to methylmercury. Dose-response relationships in a human population with dietary exposure to methylmercury at levels believed to be in the range of the threshold for developmental toxicity are being studied. Both prenatal and early postnatal body burdens of methylmercury will be examined as well as transport to the brain.

This study is testing the hypothesis, developed in previous studies of prenatal exposure in the Iraq population, that subtle psychological and behavioral changes in prenatally exposed children can be quantitatively related using dose-response models to the mother's methylmercury exposure during pregnancy. In the Seychelles, a group of islands off the coast of Africa near Madagascar, a group of 779 infants who were prenatally exposed to methylmercury through maternal fish consumption is being studied with annual administration of neurodevelopmental, psychological and educational testing of the

children through 5.5 years of age. This population consumes a relatively large amount of marine fish and marine mammals, both of which are likely to contain methylmercury. The study is testing the hypothesis that methylmercury concentration in hair correlates with methylmercury in the brain by using human autopsy data. Mechanisms of transport of methylmercury across the blood brain barrier also are being studied to understand better the factors that limit the accuracy of hair mercury as a biological marker for target tissue levels. Findings reported in recent publications are summarized in section 3.3.1.1.

The second study is the Faroe Islands Study led by Dr. P.A. Grandjean from Odense University in Denmark. The purpose of this study is to determine whether a neurotoxic risk is present from methylmercury exposure from seafood and, if so, the threshold for such effects. This study is examining a cohort of 1,000 children in the Faroe Islands, located in the North Atlantic between Scotland and Iceland. As is the case in the Seychelles, this population consumes a relatively large amount of seafood; consumption includes marine fish and marine mammals. Intrauterine exposures were determined by mercury analysis of umbilical cord blood and maternal hair collected at consecutive births during 21 months in 1986 and 1987. In 13 percent of the births, mercury levels were greater than 10 ppm in maternal hair, and 25 percent of the cord blood samples had a mercury concentration above the corresponding level of 40 µg/L. No cases of gross methylmercury poisoning have been observed. The persistence of mercury in the body is being assessed from mercury hair concentrations in the children at one and six years of age, and dietary information is being collected. A detailed pediatric examination and a test battery to identify possible subtle signs of neurobehavioral dysfunction are being conducted. The test battery includes psychological tests and neurophysiological measurement of evoked potentials; these methods are known from previous research to be particularly sensitive to the types of neurotoxicity expected.

The Faroese population was chosen for this study because of the homogeneity and stability of the population and the efficient coverage of the Danish health care system. The cohort includes 75% of all births occurring during the sampling period. A high participation rate (about 80%) is expected at the 6-year examination period. Alcohol use is minimal in Faroese women (75% were abstainers during pregnancy), and 60% are nonsmokers. The lead exposure is low (median lead concentration in cord blood was 1.7 µg/100 mL). Exposure to polychlorinated biphenyls (PCB), however, may be a confounder, and alcohol intake of the fathers may have been high. Due to the high seafood intake, selenium exposure is increased, and its possible protective action against mercury toxicity is being examined. Findings reported at recent scientific meetings are summarized in section 3.3.1.1.

## **7.2 Research Needs**

In addition to the ongoing studies described above, further research is necessary for refinement of the U.S. EPA's risk assessments for mercury and mercury compounds. In order to reduce uncertainties in the current estimates of the oral reference doses (RfDs) and inhalation reference concentrations (RfCs), longer-term studies with low-dose exposures are necessary. In particular, epidemiological studies should emphasize comprehensive exposure data with respect to both dose and duration of exposure. The current RfD and RfC values have been determined for the most sensitive toxicity endpoint for each compound; that is, the neurological effects observed following exposure to elemental or methylmercury, and the renal autoimmune glomerulonephritis following exposure to inorganic mercury. For each of these compounds, experiments conducted at increasingly lower doses with more sensitive measures of effect will improve understanding of the respective dose-response relationships at lower exposure levels and the anticipated thresholds for the respective effects in humans. Similar information from developmental toxicity studies would allow determination of RfDs for developmental toxicity (RfD<sub>dt</sub>) for elemental and inorganic mercury. For inorganic mercury, furthermore, the many ongoing studies in which mechanisms of action are being investigated will greatly assist in quantifying the risks posed by these compounds.



Well-conducted studies are also needed to clarify exposure levels at which toxic effects other than those defined as “critical” could occur in humans. For all three forms of mercury, data are inadequate, conflicting, or absent for the following: adverse reproductive effects (effects on function or outcome, including multigeneration exposure); impairment of immune function; and genotoxic effects on human somatic or germinal cells (elemental and inorganic mercury). Investigations that relate the toxic effects to biomonitoring data will be invaluable in quantifying the risks posed by these mercury compounds. In addition, work should focus on subpopulations that have elevated risk because they are exposed to higher levels of mercury at home or in the workplace, because they are also simultaneously exposed to other hazardous chemicals, or because they have an increased sensitivity to mercury toxicity. Information on postnatal exposure without prenatal exposure is limited; therefore, analyzing the potential risks associated with mercury exposure of young children is difficult.

There are data gaps in the carcinogenicity assessments for each of the mercury compounds. The U.S. EPA's weight-of-evidence classification of elemental mercury (Group D) is based on studies in workers who were also potentially exposed to other hazardous compounds including radioactive isotopes, asbestos, or arsenic. There were no appropriate animal studies available for this compound.

Studies providing information on the mode of action of inorganic mercury and methylmercury in producing tumors will be of particular use in defining the nature of the dose response relationship.

The assessment of both noncarcinogenic effects and carcinogenic effects will be improved by an increased understanding of the toxicokinetics of these mercury compounds. In particular, quantitative studies that compare the three forms of mercury across species and/or across routes of exposure are vital for the extrapolation of animal data when assessing human risk. For elemental mercury there is a need for quantitative assessment of the relationship between inhaled concentration and delivery to the brain or fetus; in particular the rate of elemental to mercuric conversion mediated by catalase and the effect of blood flow. Such assessment is needed for evaluation of the impact of mercury exposure from dental amalgam.

Work has been done on development of physiologically-based pharmacokinetic models. While one of these has developed a fetal submodel, data on fetal pharmacokinetics are generally lacking. The toxicokinetics of mercury as a function of various developmental stages should be explored. Elemental mercury and methylmercury appear to have the same site of action in adults; research is, therefore, needed on the potential for neurotoxicity in newborns when the mother is exposed. This work should be accompanied by pharmacokinetic studies and model development.

classification error, however, the results of the response-classification uncertainty analysis indicate that the late walking endpoint was unreliable as a measure of methylmercury toxicity. The exclusion of this endpoint would not have a very large impact on the combined developmental effects threshold distribution, increasing the thresholds by about 50%. Although the late talking threshold distribution is not grossly affected by response-classification error, variability in interpretation of the definition of the endpoint (first talking) likely would have been greater than that for walking; this uncertainty was not estimated in this analysis. The neurological effects thresholds were least sensitive to classification error, assuming that the true error was closer 10% than 20%. The assumption seems reasonable given the much greater objectivity of the measurement of the effect. Adult paresthesia was the most sensitive to classification error, showing extreme variability in the threshold estimates with a classification error rate as low as 5% (all observations). These results suggest that strong conclusions based on the late walking and adult paresthesia endpoints are unwarranted.

Results of the alternate scenarios (Table D-8) show that the primary effect of the correlation assumptions among the dose conversion input variables was a fairly large reduction in the variance of the Monte Carlo simulation output. The assumption of correlation of individual susceptibility and half-life of methylmercury in the blood did not have a marked effect on the simulation except for a 42% reduction in the median when a strong correlation was assumed ( $t_{1/2} > 84$  days). The latter scenario probably represented a worst-case situation although no data were found that directly address the magnitude of the hypothetical correlation.

The sensitivity analysis indicates that the variables that contribute the most to the dose conversion simulation variability are the hair:blood ratio (**hb**), the half-life of methylmercury in the blood ( $t_{1/2}$ ) and the fraction of absorbed methylmercury found in the blood (**f**). There is very little that can be done to reduce the uncertainty in these variables because appropriate data directly applicable to the Iraqi cohort are not available. These results could be of use in the experimental design and collection of data for estimates of ingestion levels from hair concentrations in the future.

#### **2.4.5 Conclusions of Analysis of Uncertainty Around Human Health effects of Methylmercury**

A major source of the variability was in the estimation of bootstrap thresholds from the Iraqi cohort data as evidenced by the 12-20 fold difference in the 5<sup>th</sup> and 95<sup>th</sup> percentiles of the bootstrap threshold distributions. The uncertainty arising from limited exposure duration contributed almost as much, with a 12.5-fold difference in the 5<sup>th</sup> and 95<sup>th</sup> percentiles. The corresponding spreads in the dose conversion distributions were 2.4-4.2 fold. Correlations between variables were important with respect to the variance of the Monte Carlo simulations but were not well-defined by empirical data. Additional areas of uncertainty remain to be modeled.

Of the developmental endpoints, the neurological effects, which are determined by a battery of tests and do not depend on subject recall, would seem to be the most objective measure of methylmercury toxicity. Late walking was not a reliable endpoint because of sensitivity to classification error.

The RfD of  $1 \times 10^{-4}$  mg/kg-day is very likely well below the threshold for developmental effects but may be above the threshold for exposure duration-adjusted adult paresthesia. Strong conclusions based on the latter result are not warranted because of the sensitivity of the adult paresthesia threshold to classification error and the general lack of data addressing the effects of exposure duration.

#### **D.5 References**



# CONSENSUS STATEMENT ON METHYLMERCURY AND PUBLIC HEALTH

## Endorsers:

\*Statement is Attached



American Public Health  
Association

# PSR<sup>®</sup>

Physicians for  
Social  
Responsibility



Children's Environmental  
Health Network

## American Academy of Pediatrics

DEDICATED TO THE HEALTH OF ALL CHILDREN™



# The Arc



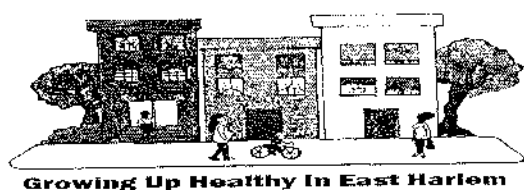
## AMERICAN NURSES ASSOCIATION

# ACPM

American College of  
Preventive Medicine



American Association on Mental Retardation



Growing Up Healthy In East Harlem

Mount Sinai School of Medicine



INSTITUTE for  
CHILDREN'S  
ENVIRONMENTAL  
HEALTH

**American Academy of Pediatrics · American Association on Mental Retardation · American College of Preventive Medicine · American Nurses Association · American Public Health Association · American Society of Autism · Association of Reproductive Health Professionals · Children's Environmental Health Network · Health Care Without Harm · Institute for Children's Environmental Health/Learning and Developmental Disabilities Initiative · Learning Disabilities Association · Mount Sinai Center for Children's Health and the Environment · National Association of County and City Health Officials · National Association of School Nurses · National Partnership for Women and Families · Physicians for Social Responsibility · Safe Minds (Sensible Action For Ending Mercury Induced Neurological Disorders) · Saratoga Foundation for Women Worldwide, Inc · The Arc of the United States · The Breast Cancer Fund**

## **State and Local Endorsing Organizations:**

Alameda County Board of Supervisor's Health Committee, California  
Alameda County Environmental Health Department, California  
Alameda County Persistent Bioaccumulative Toxicants Committee, California  
Alameda County Public Health Department, California  
Bayview Hunters Point Community Advocates, California  
Breast Cancer Action  
California Communities Against Toxics  
Catholic Healthcare West  
Center for Environmental Health  
Clean Water Action, California  
Commonweal  
Community Toolbox for Children's Environmental Health  
Department of Pediatrics, John Muir Medical Center, California  
East Bay Learning Disabilities Association of America, California  
Environmental Health Fund  
EnviroSpec  
Healthy Children Organizing Project  
Hesperian Foundation  
Institute for a Sustainable Future  
Institute for Agriculture and Trade Policy  
International Indian Treaty Council  
Kids Eat Great, Inc.  
Literacy for Environmental Justice  
Ma'at Youth Academy  
Mercury Free Minnesota  
Minnesota Public Health Association  
National Latina Health Organization  
Oregon Center for Environmental Health  
PAC/LAC - Perinatal Advisory Council: Leadership, Advocacy and Consultation  
San Francisco Medical Society  
Southern California Public Health Association  
Sprout – Berkshire Initiative for Children's Environmental Health  
Women's Voices for the Earth  
Hoosier Environmental Council  
American Academy of Pediatrics, Massachusetts Chapter  
Association of Labor Assistants and Childbirth Educators  
Boston Association for Childbirth Education (BACE)  
HealthLink

Massachusetts Nurses Association  
Maternal and Child Health Department, Boston University School of Public Health  
Division of Environmental Sciences, The Children's Hospital at Montefiore, the Albert  
Einstein College of Medicine, The Bronx, NY.  
New York City Coalition to End Lead Poisoning  
New York Committee for Occupational Safety and Health  
South Bronx Clean Air Coalition  
Ursuline Sisters of Tildonk-U.S. Province  
Learning Disabilities Association of Oregon  
Medical Society of Metropolitan Portland  
Oregon State Public Interest Research Group  
Oregon Center for Environmental Health  
Oregon Environmental Council  
Oregon Nurses Association  
Oregon Pediatric Nurse Practitioner Association  
Oregon Pediatric Society  
Oregon Toxics Alliance  
The Committee on Maternal and Perinatal Health, Texas Medical Association  
Healthy Buildings Network  
Institute for Children's Environmental Health  
Institute for Neurotoxicology and Neurological Disorders  
People for Puget Sound  
Washington State Chapter of the American Academy of Pediatrics  
Washington Toxics Coalition

### **Consensus Statement on Methylmercury and Public Health**

**As organizations representing medical and public health professionals, women, and advocates of children and families, we are concerned that the American public is not adequately protected from exposure to mercury in the environment. We call for immediate actions to protect the general public and vulnerable populations such as pregnant women and children, through stronger regulations to curb mercury emissions at their source, and through improved fish consumption guidance to reduce exposures.**

#### ***I. Our Organizations Are Concerned About the Human Health Toll from Mercury Pollution.***

***Mercury threatens human health and child development.*** Scientific findings indicate that mercury is a significant threat to the fetus, infants, and young children. Exposure to methylmercury, the highly toxic form of organic mercury found in our environment and food, may adversely affect reproduction<sup>1</sup> and a variety of organ systems, including the cardiovascular

system<sup>ii,iii</sup> and, in particular, the brain and central nervous system.<sup>iv</sup> The developing brain is more susceptible to methylmercury exposure than are adult brains, and is most sensitive while *in utero*.<sup>v</sup> Methylmercury crosses the placenta easily and readily penetrates the fetal brain.<sup>vi</sup> It is also secreted in breast milk, although the contribution of methylmercury exposure through lactation is not yet fully understood.<sup>vii</sup>

High dose exposures to methylmercury during fetal development can result in low birth weight, small head circumference, severe mental retardation, cerebral palsy, deafness, blindness, and seizures.<sup>viii</sup> Recent epidemiological studies have shown that children exposed to moderate or low levels of mercury before birth may also experience neurological and development impairment. Outcomes may include delayed walking, delayed speech, and decreased performance on tests of attention, fine motor function, language, visual-spatial abilities, and memory.<sup>ix,x,xi</sup>

The U.S. Environmental Protection Agency (EPA) has derived a "safe" level for mercury in the human body of 5.8 micrograms per liter ( $\mu\text{g/L}$ ) of blood, and a reference dose (RfD) of 0.1  $\mu\text{g}$  per kilogram of body weight per day.<sup>xii</sup> The National Academy of Sciences (NAS) has endorsed EPA's RfD, calling it a "scientifically appropriate level for the protection of public health."<sup>xiii</sup>

***The American public is exposed to methylmercury at unacceptable levels.*** Mercury released from various industrial sources eventually deposits in water bodies, where it is converted to methylmercury through microbial action and accumulates in many edible fish species. Most Americans' exposure to methylmercury comes through contaminated fish. Virtually all freshwater and ocean fish and shellfish are contaminated to varying degrees, and the range of methylmercury levels commonly found in these foods include some that pose a health risk to the public.<sup>xiv</sup>

The Centers for Disease Control and Prevention (CDC) found in January 2003 that nearly eight percent of women of child bearing ages (16 to 49) are exposed to levels of mercury that exceed the EPA RfD, considered safe for a fetus.<sup>xv</sup> A more recent analysis by EPA scientists raised that estimate to more than 15% of women, based on peer-reviewed studies showing that cord blood concentrates mercury at significantly higher levels than maternal blood.<sup>xvi</sup> Using 2000 census figures to extrapolate across the entire U.S. population, this could mean that as many as 630,000 newborns each year are at risk of serious congenital neurological and developmental impairment.

***The American public is not adequately protected from mercury pollution.*** Available data suggest that human activities have increased levels of mercury in the atmosphere by roughly a factor of 3, average deposition rates by a factor of 1.5 to 3 and deposition near industrial areas by a factor of 2 to 10.<sup>xvii</sup> Major identified sources of mercury pollution in the United States include coal-fired power plants, industrial boilers, municipal and medical waste incinerators, and chlorine manufacturing (chlor-alkali) facilities.<sup>xviii</sup>

While mercury emissions from various sources may be transported long distances in the atmosphere, local mercury sources play an important role in local pollution. Draft EPA modeling indicates that at mercury "hotspots" within the United States (locations where mercury deposition is highest), local emission sources within a state can be the dominant source of deposition. In addition, a recent 10-year study by the state of Florida points to the importance of



local mercury pollution sources and the feasibility of measures to protect public health. In that study, strict emission limits applied to incinerators in south Florida were found to produce emissions reductions of 99% and corresponding reductions in mercury levels in Everglades fish and wildlife of 60%.<sup>xix</sup>

As states have recognized the problem posed by mercury in their waters and developed improved monitoring programs, public health warnings designed to minimize the public's exposure to methylmercury-contaminated fish and shellfish have increased dramatically. State-level fish consumption advisories for mercury are up from 899 in 1993 to 2,140 in 2002 (an increase of 138 percent in total); more than 12 million lake acres and 473,000 river miles in 44 states were under advisory for methylmercury in 2002.<sup>xx</sup> At the federal level, however, consumption guidance from EPA and the Food and Drug Administration (FDA) has been fragmented, incomplete, and sometimes contradictory. In July 2002, and again in December 2003, FDA's own Food Advisory Committee recommended that existing federal guidance be strengthened to sufficiently protect public health and vulnerable populations.<sup>xxi</sup>

## ***II. We Call on Federal, State, and Tribal Leaders to Do More to Protect Public Health from Mercury.***

In light of the serious public health threat posed by exposure to methylmercury, particularly to the fetus, infant, and young child, and acknowledging the scientific consensus which supports major reductions in industrial mercury emissions as quickly as possible, we call for immediate actions to remediate the threat of mercury exposure. Therefore, policy makers at all levels should:

1. Treat mercury emissions from all anthropogenic sources as "hazardous," and rapidly implement regulations aimed at attaining the maximum achievable emissions reductions;
2. Employ protective and uniform emission limits for anthropogenic mercury sources in all communities, with no trading of mercury emissions among sources;
3. Develop comprehensive consumption guidelines for mercury in fish and seafood that is scientifically based and aimed at ensuring that 98% or more of the population – particularly women of reproductive age and children – is within EPA's "safe" level of methylmercury exposure; and
4. Cooperate internationally to reduce the global problem of mercury contamination by addressing mercury sources in all countries.

---

<sup>i</sup> Choy CM, Lam CW, Cheung LT, Britton-Jones CM, Cheung LP, Haines CJ. Infertility, blood mercury concentrations and dietary seafood consumption: a case-control study. *BJOG: an International Journal of Obstetrics and Gynecology*. 2002;109:1121-5.

<sup>ii</sup> Yoshizawa K, Rimm EB, Morris JS, Spate VL, Hsieh CC, Spiegelman D, Stampfer MJ, Willett WC, 2003. Mercury and the risk of coronary heart disease in men, *N Engl J Med*. 2002; 28;347(22):1755-60.

<sup>iii</sup> Gualler B, et. al, Mercury, fish oils, and the risk of myocardial infarction, *N Engl J Med*. 2002;347:1747-54.

- <sup>iv</sup> Sanfeliu C, Sebastia J, Cristofol R, Rodriguez-Farre E. Neurotoxicity of organomercurial compounds. *Neurotox Res.* 2003;5(4):283-305.
- <sup>v</sup> Agency for Toxic Substances and Disease Registry (ATSDR). 1999. Toxicological profile for mercury. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service. <http://www.atsdr.cdc.gov/toxprofiles/tp46.html>
- <sup>vi</sup> Myers GJ, Davidson PW. Prenatal methylmercury exposure and children: neurologic, developmental, and behavioral research. *Environ Health Perspect.* 1998 Jun;106 Suppl 3:841-7.
- <sup>vii</sup> Sakamoto M, et al. Declining risk of methylmercury exposure to infants during lactation. *Environ Res.* 2002 Nov;90(3):185-9.
- <sup>viii</sup> Kondo K. Congenital Minamata disease: warnings from Japan's experience. *J Child Neurol.* 2000 Jul;15(7):458-64.
- <sup>ix</sup> Grandjean, P., et. al. Cognitive deficit in 7-year-old children with prenatal exposure to methylmercury, *Neurotoxicology and Teratology*, 1997; 19(6):417-428.
- <sup>x</sup> Grandjean, P., et al., Methylmercury neurotoxicity in Amazonian children downstream from gold mining, *Environmental Health Perspectives*. 1999;107(7):587-591.
- <sup>xi</sup> Steuerwald, U, et al. Maternal seafood diet, methylmercury exposure, and neonatal neurologic function. *J Pediatr.* 2000 May;136(5):599-605.
- <sup>xii</sup> U.S. EPA, 1997a. Mercury Study Report to Congress, Volume V: Health Effects Of Mercury And Mercury Compounds. EPA-452/R-97-007.
- <sup>xiii</sup> Committee on the Toxicological Effects of Methylmercury, Board on Environmental Studies and Toxicology, National Research Council, National Academy of Sciences. Toxicological Effects of Methylmercury. 2000.
- <sup>xiv</sup> U. S. Food and Drug Administration, Center for Food Safety and Applied Nutrition, Office of Seafood. Mercury Levels in Seafood Species. May 2001. <http://www.cfsan.fda.gov/~drl/sea-mchg.html>.
- <sup>xv</sup> Schober SE, et al. Blood mercury levels in US children and women of childbearing age, 1999-2000. *JAMA* 2003;289(13):1667-1674.
- <sup>xvi</sup> Mahaffey KR. Methylmercury: Epidemiology Update. Slide presentation given at the National Forum on Contaminants in Fish. San Diego, CA. January 26, 2004. Accessed online March 1, 2004. <http://www.epa.gov/waterscience/fish/forum/2004/presentations/monday/mahaffey.pdf>.
- <sup>xvii</sup> From UNEP Global Assessment of Mercury, 2003 <http://www.chem.unep.ch/mercury/Report/Key-findings.htm>
- <sup>xviii</sup> U.S. EPA, 1997a. Mercury Study Report to Congress, Volume II: An Inventory of Anthropogenic Mercury Emissions in the United States. EPA-452/R-97-004.
- <sup>xix</sup> Florida Department of Environmental Protection. Integrating Atmospheric Mercury Deposition and Aquatic Cycling in the Florida Everglades: An approach for conducting a Total Maximum Daily Load analysis for an atmospherically derived pollutant, Integrated Summary, Final Report. October 2003. <http://www.floridadep.org/labs/mercury/index.htm>.
- <sup>xx</sup> U.S. EPA, Office of Water. Update: National Listing of Fish and Wildlife Advisories. May 2003. EPA-823-F-03-003. <http://www.epa.gov/ost/fish>
- <sup>xxi</sup> U. S. Food and Drug Administration. Minutes of the FDA Food Advisory Committee Meeting on Methylmercury. July 23-25, 2002. <http://www.fda.gov/ohrtms/dockets/ac/02/minutes/3872ml.pdf>.

## BEFORE THE U.S. ENVIRONMENTAL PROTECTION AGENCY

"Standards of Performance for New and Existing Stationary Sources: Electric Utility Steam Generating Units: Reconsideration," 70 Fed. Reg. 62,213 (October 28, 2005).

DOCKET OAR-2002-0056

## COMMENTS OF:

Clean Air Task Force  
Izaak Walton League of America  
Natural Resources Council of Maine  
Ohio Environmental Council  
U.S. Public Interest Research Group  
Natural Resources Defense Council  
Chesapeake Bay Foundation  
Waterkeeper  
Aroostook Band of Micmac Indians  
Houlton Band of Maliseet Indians  
Penobscot Indian Nation  
The Passamaquoddy Tribe at Indian Township

December 19, 2005

**I. Introduction and Background**

EPA's final Clean Air Mercury Rule ("CAMR") is fundamentally based on EPA's mistaken and illegal assumption that the Clean Air Act authorizes the Agency to regulate hazardous air pollutants ("HAPs") through any mechanism other than under the MACT provisions of section 112. We have previously articulated the legal problems with EPA's overall approach in our earlier comments on the proposed rule.<sup>1</sup> In addition,

---

<sup>1</sup> CATF & NRDC, Comments on Proposed National Emission Standards for Hazardous Air Pollutants; and in the Alternative, Proposed Standards of Performance for New and Existing Stationary Sources, Electric Utility Steam Generating Units: Notice of Data Availability, OAR-2002-0056 (January 3, 2005) ("NODA Comments"); CATF, NRDC, *et al.*, Comments on Proposed National Emission Standards for Hazardous Air Pollutants; and in the Alternative, Proposed Standards of Performance for New and Existing Stationary Sources, Electric Utility Steam Generating Units, OAR-2002-0056, at Chapter III (June 29, 2004) ("Comments on Proposed Rule"). EPA proposed one rule, but finalized two: a "delisting rule" and the CAMR. We are also filing today reconsideration comments on the reopened delisting rule, Comments, Revision of December 2000 Regulatory Finding on the Emissions of Hazardous Air Pollutants from



## Mercury

<http://www.epa.gov/mercury/exposure.htm>  
Last updated on Monday, September 24th, 2007.

You are here: [EPA Home](#) [Mercury](#) Human Exposure

## Human Exposure

Mercury exists in various forms, and people are exposed to each in different ways. The most common way people in the U.S. are exposed to mercury is by eating fish containing methylmercury. Other exposures may result from using or breaking products containing mercury. The [health effects](#) of these exposures are discussed in a separate section.

- ⋮ [Methylmercury](#)
- ⋮ [How mercury enters the environment](#)
- ⋮ [Moving up the food chain](#)
- ⋮ [Elemental mercury](#)
- ⋮ [Other mercury compounds](#) (inorganic and organic)

### Information for...

Businesses  
Consumers  
Health Care Providers  
Parents  
Schools

### Basic Information

Frequent Questions  
Health Effects  
Fish Consumption Advisories

People who use [mercury in the workplace](#) need to take special precautions.

## Methylmercury exposure

Outbreaks of methylmercury poisoning have made it clear that adults, children, and developing fetuses are at risk from dietary exposure to methylmercury. During these poisoning outbreaks some mothers with no symptoms of nervous system damage gave birth to infants with severe disabilities and it became clear that the developing nervous system of the fetus may be more vulnerable to methylmercury than is the adult nervous system. Mothers who are exposed to methylmercury and breast-feed their babies may also expose their infant children through their milk.

In 2004 EPA and FDA issued the first-ever joint consumer advice about methylmercury in fish and shellfish. This advice was for women who might become pregnant; women who are pregnant; nursing mothers; and young children. The advisory provides three recommendations for selecting and eating fish or shellfish to ensure that women and young children will receive the benefits of eating fish and shellfish and be confident that they have reduced their exposure to the harmful effects of methylmercury. EPA also hosts a web-based compilation of fish advisories issued by States, tribes, territories and local governments. [Fish Consumption Advisories](#)

Recent human biological monitoring by the [Centers for Disease Control and Prevention in 1999 and 2000 \(PDF\)](#) (3 pp., 42 KB, [About PDF](#)) shows that most people have blood mercury levels below a level (5.8 µg/L of whole blood) associated with possible health effects. Consumption of fish with higher methylmercury levels can lead to elevated levels of mercury in the bloodstream of unborn babies and young children and may

### Terms Defined

**Reference Dose (RfD):** An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive

harm their developing nervous system. These disabilities have been documented in ability to use language, to process information, and in visual/motor integration. U.S. EPA's 2001 Reference Dose (RfD) for methylmercury was calculated to protect the developing nervous system. Currently, U.S. EPA uses a RfD of 0.1 µg/kg body weight/day as an exposure without recognized adverse effects. A description of EPA's Reference Dose for methylmercury may be found at <http://www.epa.gov/iris/subst/0073.htm>.

In U.S. EPA's Mercury Study Report to Congress (1997) EPA estimated that 7% of women of childbearing age would have blood mercury concentrations greater than those equivalent to the RfD. The estimate of 7% of women of childbearing age above the RfD was based on patterns of fish and shellfish consumption and methylmercury concentrations present in fish and shellfish. Blood mercury analyses in the 1999-2000 National Health and Nutrition Examination Survey (1999-2000 NHANES) for 16-to-49 year old women showed that approximately 8% of women in the survey had blood mercury concentrations greater than 5.8 ug/L ( which is a blood mercury level equivalent to the current RfD). Based on this prevalence for the overall U.S. population of women of reproductive age and the number of U.S. births each year, it is estimated that more than 300,000 newborns each year may have increased risk of learning disabilities associated with in utero exposure to methylmercury. More recent data from the CDC support this general finding.

Nearly all methylmercury exposures in the U.S. occur through eating fish and shellfish. Microscopic organisms convert inorganic mercury into methylmercury, which accumulates up the food chain in fish, fish-eating animals, and people.

This process is explained below.

- ∴ [How mercury enters the environment](#)
- ∴ [Moving up the food chain](#)

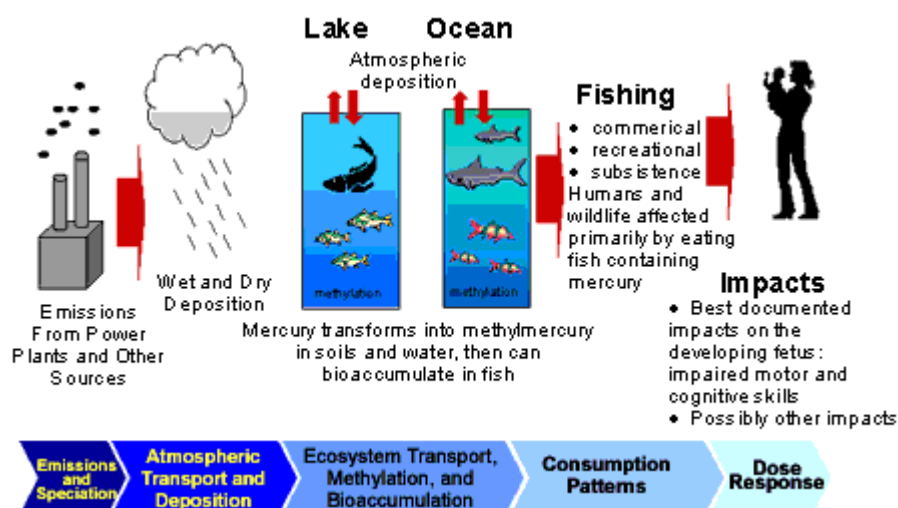
subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. It can be derived from a NOAEL, LOAEL, or benchmark dose, with uncertainty factors generally applied to reflect limitations of the data used. Generally used in EPA's noncancer health assessments.

**No-Observed-Adverse-Effect Level (NOAEL):** The highest exposure level at which there are no biologically significant increases in the frequency or severity of adverse effect between the exposed population and its appropriate control; some effects may be produced at this level, but they are not considered adverse or precursors of adverse effects.

**Lowest-Observed-Adverse-Effect Level (LOAEL):** The lowest exposure level at which there are biologically significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group

---

## How mercury enters the environment



Mercury is emitted to the air by human activities, such as manufacturing or burning coal for fuel, and from natural sources, such as volcanos.

Typically, mercury is released into the atmosphere in one of three forms:

- ⌘ elemental mercury: can travel a range of distances, may remain in the atmosphere up to one year and may travel globally before undergoing transformation
- ⌘ particle-bound mercury: can fall out of the air over a range of distances
- ⌘ oxidized mercury (sometimes called ionic or reactive gaseous mercury (RGM)): found predominantly in water-soluble forms, which may be deposited at a range of distances from sources depending on a variety of factors including topographic and meteorologic conditions downwind of a source.

What happens to mercury after it is emitted depends on several factors:

- ⌘ the form of mercury emitted
- ⌘ the location of the emission source
- ⌘ how high above the landscape the mercury is released (e.g., the height of the stack)
- ⌘ the surrounding terrain
- ⌘ the weather.

Depending on these factors, atmospheric mercury can be transported over a range of distances before it is deposited, potentially resulting in deposition on local, regional, continental and/or global scales. Mercury that remains in the air for prolonged periods of time and travels across continents is said to be in the "global cycle."

Recent emissions estimates of annual global mercury emissions from all sources, natural and anthropogenic (human-generated), which are highly uncertain, are about 4800-8300 tons per year.

U.S. anthropogenic mercury emissions are estimated to account for roughly 3 percent of the total global emissions, and the U.S. power sector is estimated to account for about 1 percent of the total global emissions. EPA has estimated that about one third of U.S. emissions are deposited within the contiguous U.S. and the remainder enters the global cycle.

Current estimates are that less than half of all mercury deposition within the U.S. comes from U.S. sources, although deposition varies by geographic location. For example, compared to the country as a whole, U.S. sources represent a greater fraction of the total deposition in

parts of the Northeast because of the direction of the prevailing winds.

---

## Moving up the food chain

When mercury falls in rain or snow, it may flow into bodies of water like lakes and streams. When it falls out of the air as dry deposition, it may eventually be washed into those bodies by rain. Bacteria in soils and sediments convert mercury to methylmercury. In this form, it is taken up by tiny aquatic plants and animals. Fish that eat these organisms build up methylmercury in their bodies. As ever-bigger fish eat smaller ones, the methylmercury is concentrated further up the food chain. This process is called "bioaccumulation".

Methylmercury concentrations in fish depend on many factors, including mercury, the concentration in water, water pH and temperature, the amount of dissolved solids and organic matter in the water, and what organisms live in the water. Methylmercury concentrations in fish may also be affected by the presence of sulfur and other chemicals in the water. Because of these variables, and because food webs are very complex, bioaccumulation is hard to predict and can vary from one water body to another.

However, in a given water body, the highest concentrations of methylmercury are generally found in large fish that eat other fish. The concentrations of methylmercury in large fish can be over a million-fold larger than in the surrounding water. EPA discussions of estimates bioaccumulation can be found in Chapter 6 and Appendix A of the Water Quality Criterion for the Protection of Human Health: Methylmercury.



---

## Elemental mercury exposure

When elemental mercury is spilled or a device containing mercury breaks, the exposed elemental mercury can evaporate and become an invisible, odorless toxic vapor. This is especially true in warm or poorly-ventilated rooms or spaces. Sources of potential exposure to elemental mercury are described below.

- ⌘ Elemental or metallic mercury is the liquid metal used in thermometers, barometers, and thermostats and other electrical switches. Metallic mercury is often found in school laboratories as well as in thermometers, barometers, switches, thermostats, and other devices found in school science labs.
- ⌘ It is not uncommon for children to break fever thermometers in their mouths. Mercury that is swallowed in such cases poses low risk comparison to the risk of breathing mercury vapor.
- ⌘ There are some necklaces imported from Mexico that contain a glass pendant that contains mercury. The mercury-containing pendants can come in various shapes such

as hearts, bottles, balls, saber teeth, and chili peppers. If broken, they release metallic mercury to the environment.

Mercury is used in dentistry in dental amalgam. Dental amalgam is a direct filling material used in restoring teeth. It is made up of approximately 40-50% mercury, 25% silver and 25-35% a mixture of copper, zinc and tin. Amalgam use is declining because the incidence of dental decay is decreasing and because improved substitute materials are now available for certain applications. The Centers for Disease Control and Prevention (CDC) reports that, at present, there is scant evidence that the health of the vast majority of people with dental amalgam is compromised, nor that removing amalgam fillings has a beneficial effect on health. More information is available at:

<http://www.cdc.gov/oralhealth/factsheets/amalgam.htm>

**Ritual Use of Mercury** - Persons who use metallic mercury in ethnic folk medicine and for religious practices may be at risk of exposure to mercury. Metallic mercury is sold under the name "azogue" in stores (sometimes called botanicas), which specialize in religious items used in Esperitismo (a spiritual belief system native to Puerto Rico), Santeria (a Cuban-based religion that venerates both African deities and Catholic saints), and voodoo. The use of azogue in religious practices is recommended in some Hispanic communities by family members, spiritualists, card readers, and santeros. Typically, azogue is carried on one's person in a sealed pouch prepared by a spiritual leader or sprinkled in the home or automobile.

---

## Exposure to other mercury compounds (inorganic and organic)

Inorganic mercury compounds take the form of mercury salts. They are generally white powders or crystals, with the exception of mercuric sulfide (cinnabar) which is red. Inorganic compounds and organic compounds (such as phenylmercury acetate and ethylmercury), have been commonly used as fungicides, antiseptics or disinfectants. They have also been used in a variety of products. Most of these uses have been discontinued, but small amounts of these compounds can still be found as preservatives in some medicines. The U.S. Food and Drug Administration maintains a [list of medicines that contain mercury](#).

Excessive exposure to inorganic and organic mercury compounds can result from misuse or overuse of mercury-containing products, especially outdated products containing more mercury. Exposure to mercury compounds is primarily through ingestion, but can occur through other pathways. Ingested organic mercury compounds are more readily absorbed through the gastrointestinal tract than are inorganic compounds.



# *Methylmercury: Epidemiology Update*

Kathryn R. Mahaffey, Ph.D.  
U.S. Environmental Protection Agency  
Washington D.C.

*Fish Forum – San Diego - 2004*

## **Reports in 2003/2004 . . .**

- 1999-2000 NHANES organic blood Hg
- *Close association with fish intake in 1999-2000 NHANES examinees.*
- Confirmation of cord blood [Hg] : adult blood [Hg] in Japanese.
- *Estimate at least 300,000 newborns in US each year with in utero blood [Hg] greater than 5.8 µ/L.*

## Reports in 2003/2004 (*continued*)

- Seychelles cohort update.
- *Methylmercury-associated adult neuro-psychological changes at hair [Hg] < 50 ppm.*
- Distribution of omega-3 fatty acids (EPA and DHA) in fish and shellfish vs. [Hg] in fish and shellfish.

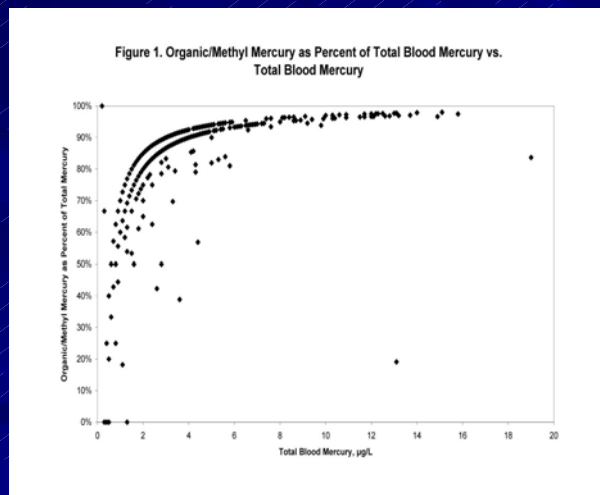
## 1999-2000 NHANES Blood Mercury

- Blood organic mercury (i.e., methylmercury) among 1709 women of childbearing age representative of US population.
- *Overall, 9% of women consumed fish at least once a week. Fish consumption higher among women over age 30 and among Asians and people of "Island" ethnicity.*

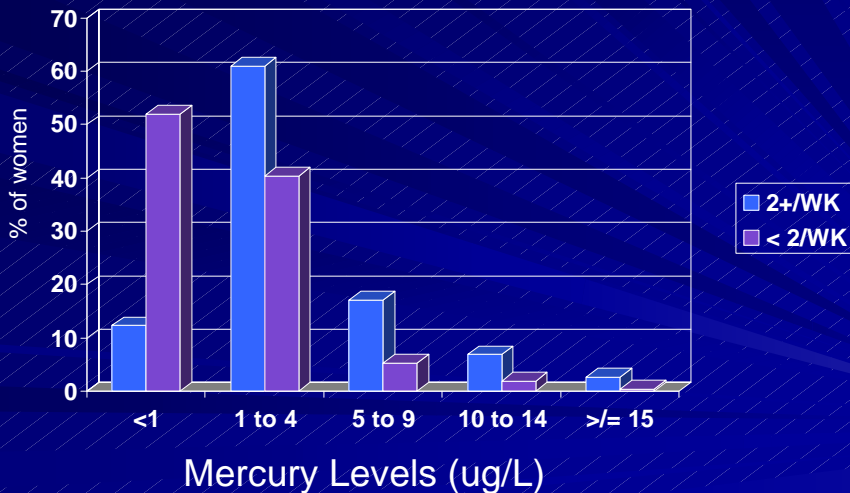
# 1999-2000 NHANES Blood Mercury

- Association:  $R = 0.5$  to  $0.6$  between dietary total mercury and blood organic mercury (Mahaffey et al., 2003).
- Blood mercury concentrations were 7 X higher among women who reported eating 9+ fish/shellfish meals within past 30 days (i.e., 2 or more times per week) compared with women who reported no fish/shellfish consumption in the past 30 days (Mahaffey et al., 2003).

## Methylmercury as a Percent of Total Blood Mercury: 1999-2000 NHANES Adult Women of Childbearing Age



## Total Mercury Levels in Women, Aged 16-49 by Weekly Fish Consumption Levels



## Basis for Uncertainty Factor of 10 in the Reference Dose for Methylmercury

### Three-fold for toxicokinetics:

#### ■ Basis for the UF of 10:

Variability and uncertainty in estimating an ingested mercury dose from cord blood mercury concentration.

Cord:maternal ratio for blood [Hg] ranges from > 3 to less than 1. Average ~ 1.7 to 1.8. New Japanese data indicate ratio of 1.6 for cord : maternal pairs.

Three-fold for toxicodynamics and uncertainty.

## Estimated Number of Newborns with In Utero Methylmercury Exposures $\geq$ RfD

- Number of US births in 2000: 4,058,814 (*National Vital Statistics Reports*).
- 1 : 1 ratio of cord to maternal blood [Hg], i.e., 5.8 cord to 5.8 maternal, 7.8% of women had total blood [Hg]  $\geq$  5.8, ~ 300,000 newborns each year  $> 5.8$  ug/L (Mahaffey et al., 2003).
- 1.7 : 1 ratio of cord to maternal blood [Hg], i.e. 5.8 cord to ~ 3.5 maternal, 15.7% of women had total blood [Hg]  $\geq$  3.5 ug/L, ~ 630,000 newborns each years  $\geq 5.8$  ug/L cord blood.

[Note: this estimate is preliminary in nature, and is based on recently available information about mercury in umbilical cord blood versus maternal blood. This new information was presented as part of an ongoing scientific dialogue on how best to understand mercury exposures. EPA is still reviewing these new studies and their potential implications. This recalculation does not impact or change the established Reference Dose (RfD); rather this work focuses solely on an exposure estimate.]

## 2003/2004 Reports on Neuropsychological Evaluations of Methylmercury Toxicity

- **Myers et al. 2003.** Seychelles cohort update (Lancet). Continued to observe no adverse effects of methylmercury exposure under the circumstances present in the Seychelles Islands.
- **Yokoo et al. 2003.** *Reduced function on tests of fine motor speed and dexterity and on tests of verbal memory among adult Amazonian villagers exposed to methylmercury.*
- **Beuter and Edwards, 2003.** Cree Indians. Additional studies among adults showed difficulty with accuracy and sharpness of visual fixation and pursuit in dynamic eye movements.

## Emerging Question on Adult Neurotoxic Effects of Methylmercury Exposures

WHO proposed threshold for adult neurotoxicity based on 5% prevalence of paresthesias at 50 ppm hair mercury (1990).

No physiological basis to assume there are no effects at lower exposures

Dose-response at lower levels needs to be determined.

## Mercury and Omega-3 Fatty Acids

- In 2003 additional epidemiology data raised more interest in mercury as a cardiac toxin.
- *Omega-3 fatty acids in fish frequently cited as a health benefit of fish and shellfish intake.*
- Key piece of information is that there are substantial species-specific differences in the distribution of mercury and of the omega-3 fatty acids.
- *Species high in mercury are not necessarily high in omega-3s and species high in omega-3s are not necessarily higher in mercury.*



## Comparison of Mercury (ppm) and Omega-3 Fatty Acid (g/100g) in Fish Species

### ■ High Mercury Species

Tilefish: 1.6 Hg, 0.17 O-3s

Shark: 1.3 Hg, 0.07 O-3s

King Mackerel: 0.97Hg,  
0.18 O-3s

Swordfish: 0.95 Hg, 0.58  
O-3s

### ■ High Omega-3 Species

Mackerel: 0.08 Hg, 3.61 O-  
3s

Salmon-sockeye: 0.03 Hg,  
3.00 O-3s

Herring: 0.01 Hg, 2.34 O-  
3s

Tuna, albacore: 0.26 Hg,  
2.33 O-3s

## Variation in Mercury and Omega-3 Fatty Acids in Fish and Shellfish

- Mercury concentrations range from < 0.02 ppm Hg in shellfish such as abalone to several ppm Hg in large predatory fish.
- *Omega-3 fatty acids (combined EPA and DHA) range from < 0.1 gram/100 grams of fish (e.g., shark species) to > 3.5 grams/100 grams of fish (mackerel species).*
- There is minimal association between the omega-3 fatty acid concentration in the fish species and the mercury concentration in the species.

## Upcoming Meeting

- Meeting on medical issues related to mercury exposure.
- Orlando, Florida
- April – 2004
- Sponsored by US EPA and US HHS in conjunction with multiple medical associations.





# ***Preliminary Results from Steubenville Hg Deposition Source Apportionment Study***

Briefing for Tim Oppelt  
April 27, 2005

Presented by Tim Watkins, NERL  
Research conducted by Matt Landis, Gary Norris, and David Olson  
in collaboration with the University of Michigan

# Purpose

- Provide a “Heads-Up” of the significant preliminary findings of the Steubenville study
  - Scientifically and Politically significant
- Seeking guidance on how to proceed with review and release of study results



# Results

- Approximately 70% of Hg wet deposition at Steubenville site is attributable to local/regional fossil fuel (coal and oil) combustion sources
  - Not entirely attributable to electric utilities
- Preliminary results
  - Additional analysis to finalize results will be completed within a month



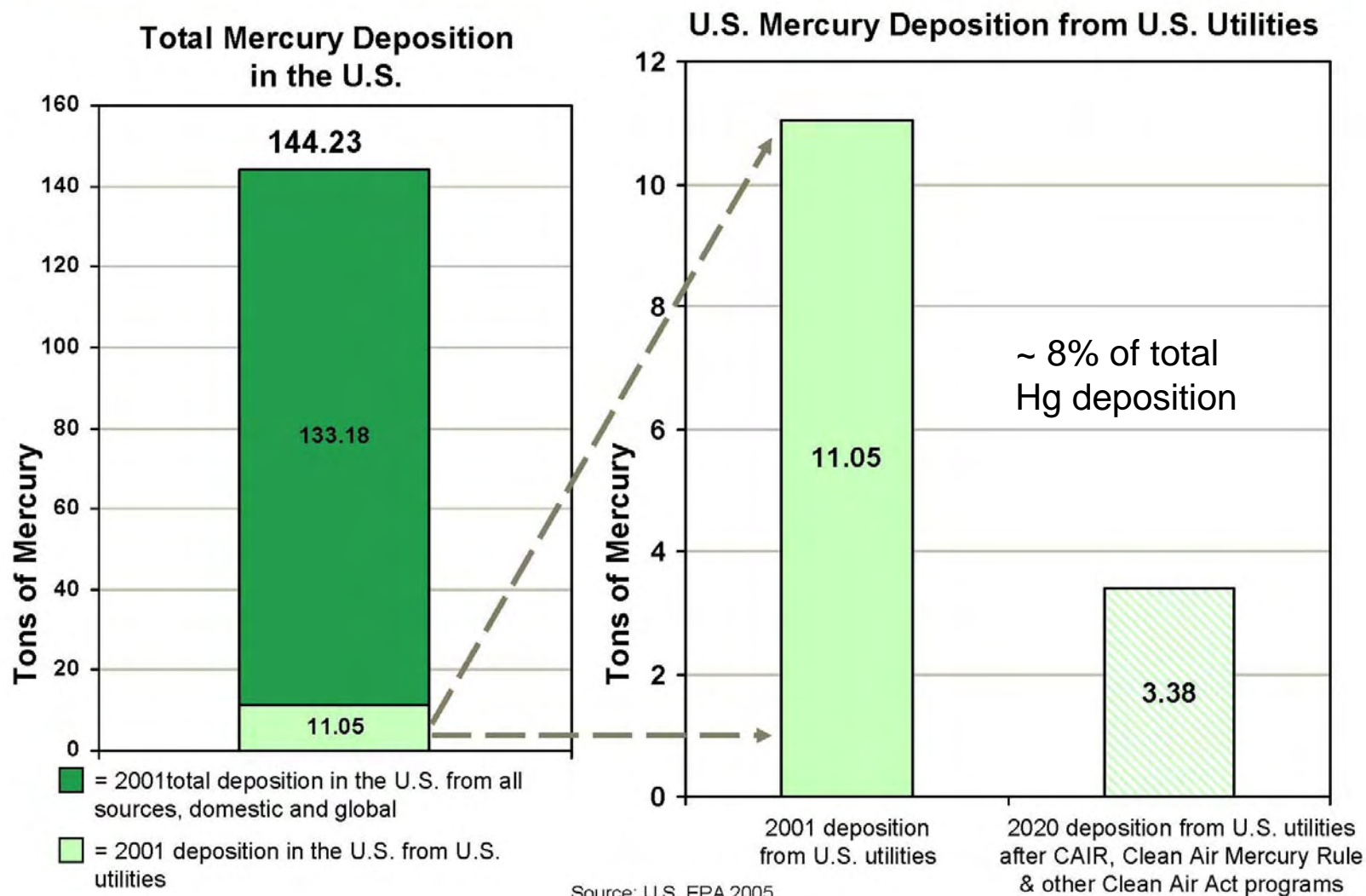
# *Significance of Results*

- Current models (including those used by EPA for CAMR analyses) estimate a much lower local/regional source contribution to Hg deposition, on average
  - On average, approximately 8% of domestic Hg deposition estimated to be from domestic electric utility coal combustion
- Implications for potentially vulnerable areas (i.e., “Hotspots”)
- Significant deposition decreases predicted for Steubenville area





# Mercury Deposition in the U.S.



Source – US EPA Clean Air Mercury Rule website (8% note added)

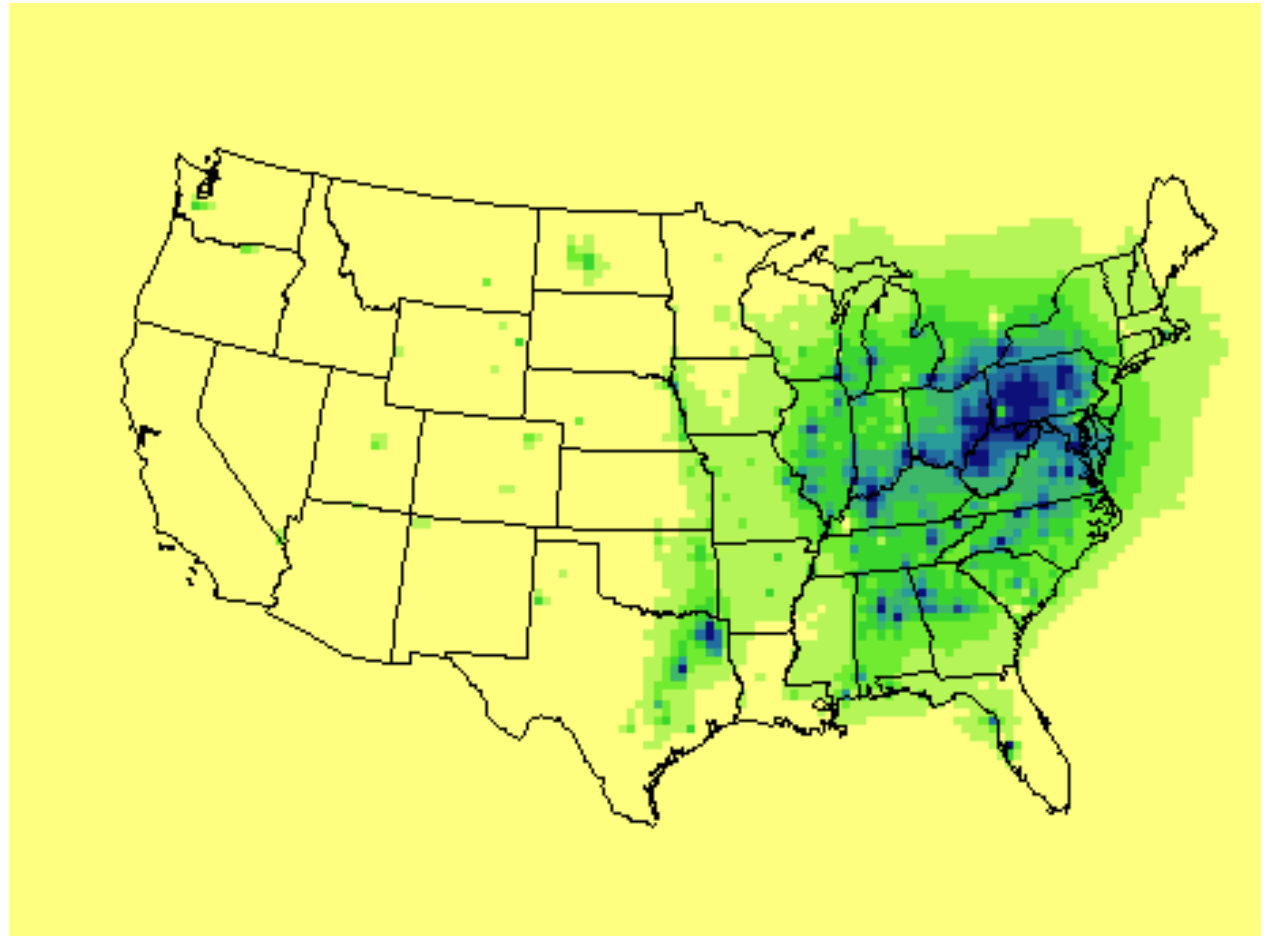
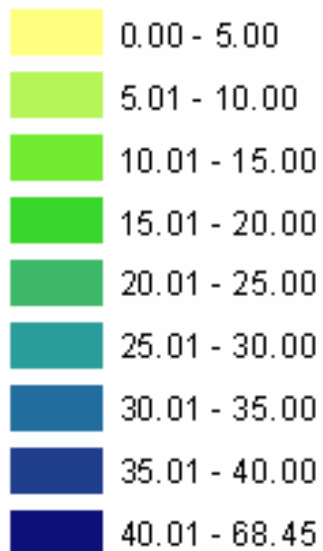


RESEARCH & DEVELOPMENT

*Building a scientific foundation for sound environmental decisions*

# *Percent Change in Deposition from a 100% Reduction of Utility Emissions*

## **Percent Change in Deposition**





## *Explanation of Results*

# *Are these results plausible?*

- Yes
  - Steubenville site was chosen as because it was anticipated to be impacted by coal combustion
  - Results would appear to contradict EPRI claims of RGM to elemental Hg plume conversion

Note: Mercury is emitted from combustion sources in one of three species – reactive gaseous mercury (RGM), particulate mercury, and elemental mercury. RGM and particulate mercury contribute to local/regional deposition, while elemental mercury tends to be transported longer distances.





# *Why haven't similar results been presented previously?*

- Recent convergence of newly available tools
  - New collection method
    - Precipitation-event-based sampler
  - Improved analytical method
    - Extremely low detection limits for trace elements
    - Use to measure potential co-pollutants (e.g., sulfur, selenium, vanadium)
  - State-of-the-art EPA receptor modeling tools
    - Statistical tools to identify relative source contributions
    - New releases of EPA UNMIX and Positive Matrix Factorization (PMF)
- Current mercury monitoring efforts do not collect data needed to conduct this type of analysis
  - Mercury Deposition Network (MDN) not designed for source apportionment studies
    - Weekly instead of event-based samples
    - In general, no co-located trace element measurements
- First time that state-of-the-art receptor models have been applied to mercury precipitation data



## *Are the results consistent with other studies?*

- Consistent with studies conducted in south FL, but . . .
  - Local deposition was attributed to municipal and medical waste incinerators
  - Used more simplistic source apportionment tool

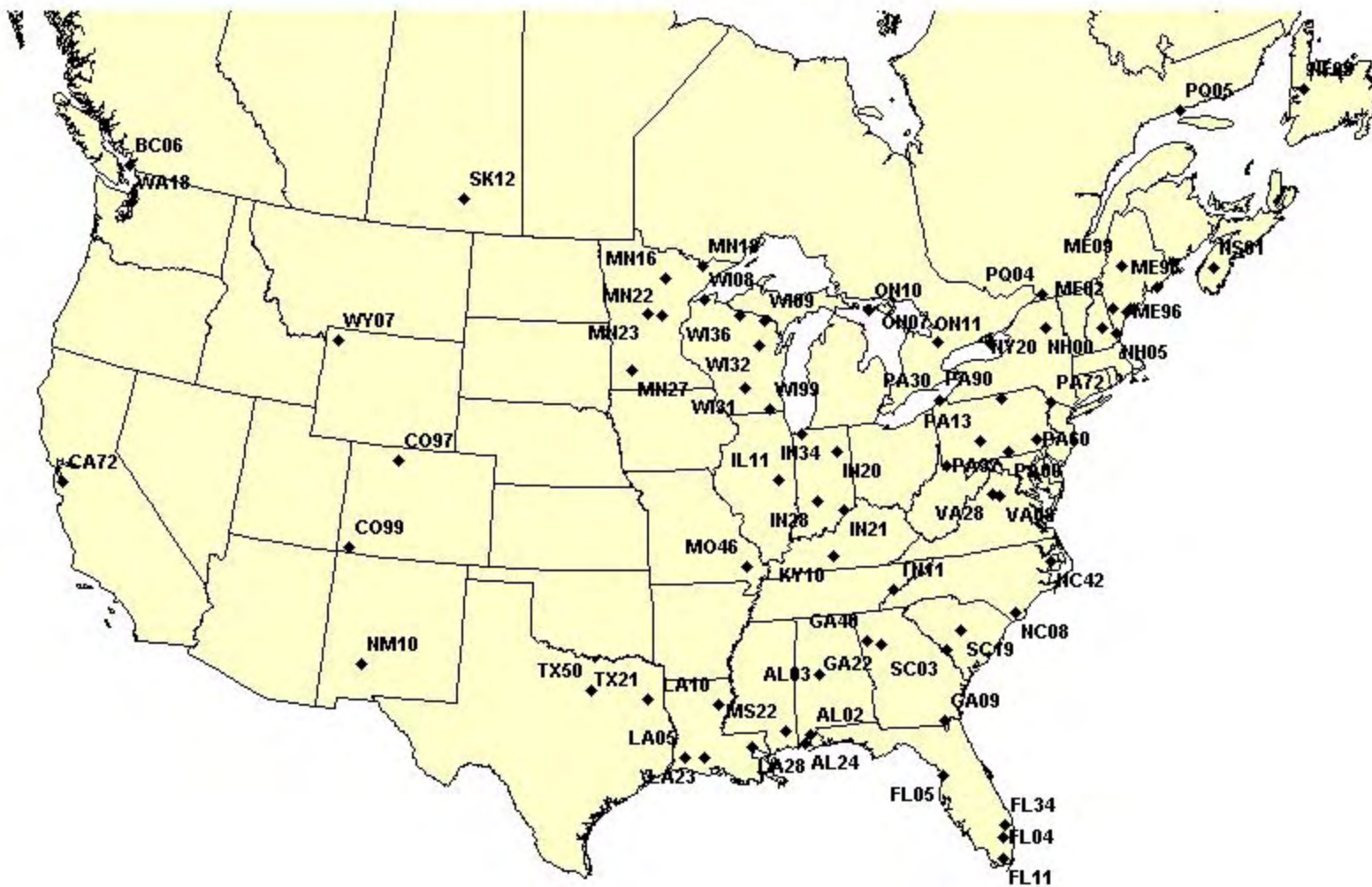


# *Why are estimated regional/local deposition values higher than those predicted in current air quality models?*

- Lack of event-based empirical deposition data for model evaluation
- Deposition parameters in current models based and evaluated against Mercury Deposition Network (MDN) data
  - MDN sites generally located in rural areas
  - Emerging but limited empirical evidence of very high Hg concentrations/deposition in urban areas
    - Chicago, Charlotte, St. Louis, and Detroit
  - Potential underestimate of predicted deposition



**National Atmospheric Deposition Program  
Mercury Deposition Network**



# *Why weren't these results available for CAMR analyses?*

- Mercury MYP included 2004 APM
  - Initial efforts to run receptor models with one-year data set (2003) were not conclusive
  - APM delayed
- Completed second year of data collection (including QA/QC) in early April 2005
- Receptor models now producing conclusive results with two-year (2003 and 2004) data set



# *Will these results be replicated?*

- Yes, because new tools are available and in use
  - New collection method
    - Developed by University of Michigan
    - Applied in Steubenville, at several other sites in Michigan, at one site in Vermont, and in Tampa, FL
  - Improved analytical method
    - University of Michigan has this capability
  - State-of-the-art receptor models
    - New EPA Receptor models are publicly available





# *Michigan Mercury Monitoring Sites Operated by the University of Michigan*



**Figure 1. Location of Atmospheric Mercury Monitoring Sites in Michigan.**



# *Planned Next Steps*

- Additional data analyses
  - Complete review of receptor modeling to finalize study results
  - Refined analyses of peak events
    - Explore meteorology data
    - Identify specific source regions and/or sources contributing to deposition events in Steubenville
- Prepare materials for EPA (OAR in particular) dissemination
- Prepare manuscript for peer-reviewed journal submission
- Future work
  - Conduct similar studies in other existing locations
    - North-South gradient in Ohio Valley (data from Univ of Mich)
    - East-West gradient using sites in Vermont (data from Univ of Mich)
    - Tampa, FL
  - Extend analysis to mercury dry deposition
  - Continue monitoring in Steubenville
    - Location for Clean Air Mercury Rule (CAMR) Accountability?
  - Integrate results into air quality models (CMAQ)





# *Issues for Discussion*

- How and when should we disseminate the results of this study within EPA (particularly to OAR)?
- Do we need to utilize additional peer-review mechanisms beyond journal submission and review?





# *Supplemental Information*

- Steubenville Study Approach
- An Overview of source apportionment
- Additional information on new source apportionment tools
  - 1) New event-based collection method
  - 2) Improved analytical method
  - 3) State-of-the-art receptor models

# *Study Approach*

- Site location / duration
  - Steubenville, OH – anticipated to impacted by coal combustion sources
  - 4-year study
    - 2-years of data collected to date (2003 and 2004)
- Cooperative agreement with the University of Michigan
- Collecting detailed measurements
  - Precipitation event-based deposition sampling
  - Potential source co-pollutants (trace elements)
  - Meteorology
- Applying state-of-the-art receptor models
  - Latest version of EPA models – UNMIX and PMF
  - First time modeling approaches applied to Hg precipitation data



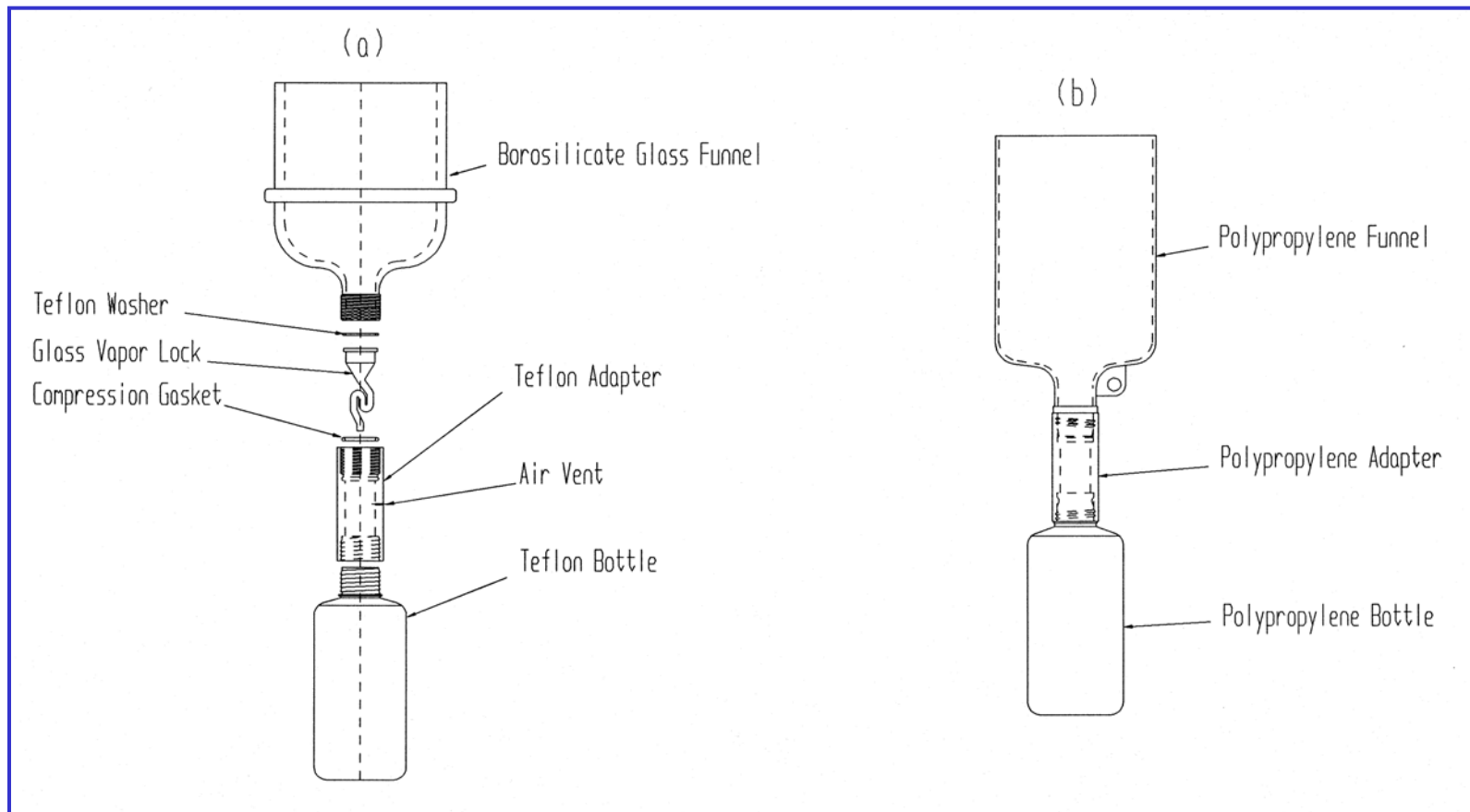
# *An Overview of Source Apportionment*

- Relating source emissions to their quantitative impact on environmental concentrations (i.e., ambient or deposition) is referred to as source apportionment
- Two approaches to source apportionment
  - Dispersion modeling (e.g., CMAQ)
    - Combines emissions, chemistry, and meteorology information to relate sources to predicted ambient concentrations
  - Receptor modeling
    - Uses environmental measurements and statistics to identify sources or source categories impacting the receptor.
- Single-sample receptor models
  - Require source profiles or “fingerprints”
  - Example – Chemical Mass Balance (CMB)
- Multivariate receptor models
  - Require many samples (100 or more)
  - Source profile information not needed
  - Examples – UNMIX and Positive Matrix Factorization (PMF)



# New Precipitation-event-based Collection Method

## Wet-Only Precipitation Collection



\* Landis and Keeler *Environ. Sci. Technol.*, **1997**, 31, 2610-2615

# Improved Analytical Methodology

## High Resolution ICP-MS Capability (Precipitation & Aerosol Samples)

- Low Resolution
  - Li, Be, Rb, Sr, Mo, Ag, Cd, In, Sn, Sb  
Cs, Ba, La, Ce, Nd, Sm, W, Tl, Pb, U
- Medium Resolution
  - Na, Mg, Al, P, S, Ca, Sc, Ti, V, Cr  
Mn, Fe, Co, Ni, Cu, Zn
- High Resolution
  - K, As, Se
- Stable Isotope Ratios
  - Pb





# State-of-the-art Receptor Models

## Statistical Receptor Model Development

- **UNMIX**
  - Multi-linear model (Ron Henry – USC)
  - Usually requires at least 100 samples
  - Does not use data below MDL
  - Generates source profiles and uncertainties
- **Positive Matrix Factorization (PMF)**
  - Multi-linear model (Phil Hopke – Clarkson University)
  - Usually requires at least 100 samples
  - Uses data below MDL
  - Incorporates uncertainties and weights individual data points
  - Generates source profiles and uncertainties



## Sources of Mercury Wet Deposition in Eastern Ohio, USA

GERALD J. KEELER,\*<sup>1</sup>  
MATTHEW S. LANDIS,<sup>1</sup> GARY A. NORRIS,<sup>1</sup>  
EMILY M. CHRISTIANSON,<sup>1</sup> AND  
J. TIMOTHY DVONCH<sup>2</sup>

*The University of Michigan Air Quality Laboratory, Ann Arbor, Michigan 48109, and U.S. EPA Office of Research and Development, Research Triangle Park, North Carolina 27709*

In the fall of 2002, an enhanced air monitoring site was established in Steubenville, Ohio as part of a multi-year comprehensive mercury monitoring and source apportionment study to investigate the impact of local and regional coal combustion sources on atmospheric mercury deposition in the Ohio River Valley. This study deployed advanced monitoring instrumentation, utilized innovative analytical techniques, and applied state-of-the-art statistical receptor models. This paper presents wet deposition data and source apportionment modeling results from daily event precipitation samples collected during the calendar years 2003–2004. The volume-weighted mean mercury concentrations for 2003 and 2004 were 14.0 and 13.5 ng L<sup>-1</sup>, respectively, and total annual mercury wet deposition was 13.5 and 19.7  $\mu\text{g m}^{-2}$ , respectively. Two new EPA-implemented multivariate statistical models, positive matrix factorization (PMF) and Unmix, were applied to the data set and six sources were identified. The dominant contributor to the mercury wet deposition was found by both models to be coal combustion (~70%). Meteorological analysis also indicated that a majority of the mercury deposition found at the Steubenville site was due to local and regional sources.

### Introduction

Mercury (Hg) is a persistent, bioaccumulative toxic pollutant. Once Hg is released into the environment, it can be converted to the organic form, methylmercury (MeHg) and then bioaccumulate in organisms within the food chain, such as fish, posing a consumption risk to wildlife and humans. In the Great Lakes Region, atmospheric deposition is widely considered to be the primary pathway for Hg into aquatic and terrestrial ecosystems (1, 2). Mercury is emitted into the atmosphere through both natural and anthropogenic processes with 50–75% of global emissions attributed to anthropogenic sources (3, 4). Major anthropogenic sources of mercury to the atmosphere include fossil fuel combustion, waste incineration, iron-steel production, coke and lime production, hazardous waste recycling, non-ferrous metal smelting, petroleum refining, and mercury cell chlor-alkali plants (5, 6).

While natural emissions of Hg are primarily in the gaseous elemental form (Hg<sup>0</sup>), combustion processes release Hg in

three major forms: Hg<sup>0</sup>, divalent reactive gaseous Hg (RGM), and particulate Hg (Hg(p)). RGM and Hg(p) are more efficiently deposited on local and regional scales near major sources because of their solubility and affinity for surface reactions, which results in much shorter atmospheric lifetimes (4). Researchers in both the U.S. and Europe have observed significant mercury deposition gradients with maximums found near urban and industrial areas (6–9) highlighting the importance of near field deposition enhancement in proximity to large anthropogenic sources. Deposition of atmospheric Hg at any particular location is therefore a complex combination of local, regional, and global emissions as well as transport, transformation, and deposition processes (4).

In a 1998 report to Congress, the U.S. Environmental Protection Agency (EPA) identified coal-fired utility boilers as the largest source of domestic anthropogenic mercury emissions to the atmosphere and provided evidence of a causal link between such releases and the presence of methylmercury in fish tissue (9). At that time, EPA recognized that the Ohio River Valley contained a high density of coal-fired utility boilers and that monitoring of atmospheric mercury deposition was not being conducted in this area. In 1999, EPA initiated planning for a mercury monitoring and source apportionment study to investigate the impact of local and regional coal combustion sources on atmospheric mercury deposition in the Ohio River Valley.

The Clean Air Mercury Rule (CAMR) was subsequently promulgated by the EPA in 2005 and established the first U.S. regulation to control mercury emissions from coal-fired utility boilers (10). CAMR uses a cap and trade approach under which utilities can buy and sell allotments in a national emissions market. Under CAMR, an interim national cap of 38 tons y<sup>-1</sup> becomes effective in 2010 and a final cap of 15 tons y<sup>-1</sup> becomes effective in 2018. The 2010 interim cap is based on mercury reductions expected to be achieved as a co-benefit from the EPA Clean Air Interstate Rule, also promulgated by EPA in 2005, which requires utilities to install controls to reduce NO<sub>x</sub> and SO<sub>2</sub>.

The relative importance of domestic coal combustion sources to atmospheric Hg deposition in the U.S. and the efficacy of the CAMR cap and trade approach to decrease Hg in fish is the topic of ongoing debate in the scientific community. At the center of this debate is the question of the relative importance of Hg emissions from domestic coal-fired utility boilers to atmospheric deposition into sensitive aquatic and terrestrial ecosystems. As part of the CAMR development process, EPA used the Community Multi-Scale Air Quality model (CMAQ), an Eulerian dispersion model, to estimate the impact of domestic mercury sources on atmospheric deposition for CY2001. While extremely useful, all contemporary deterministic models (e.g., CMAQ) are currently limited by the substantial uncertainties in emission inventories, atmospheric Hg chemistry, and wet and dry deposition parametrizations. Receptor models differ from deterministic models in that they only rely upon speciated wet deposition samples collected at a monitoring location or receptor. Deterministic and receptor modeling source apportionment approaches are independent and complementary.

Multivariate statistical receptor models, such as principal component analysis (PCA), have been successfully used to apportion the sources of Hg deposited in South Florida (11) and the sources of other chemical compounds elsewhere (12). More recently, statistical approaches such as Unmix (13) and positive matrix factorization (PMF) have been

\* Corresponding author phone: (734) 936-1836; fax: (734) 764-9424; e-mail: jkeeler@umich.edu.

<sup>1</sup> The University of Michigan Air Quality Laboratory.

<sup>2</sup> U.S. EPA Office of Research and Development.



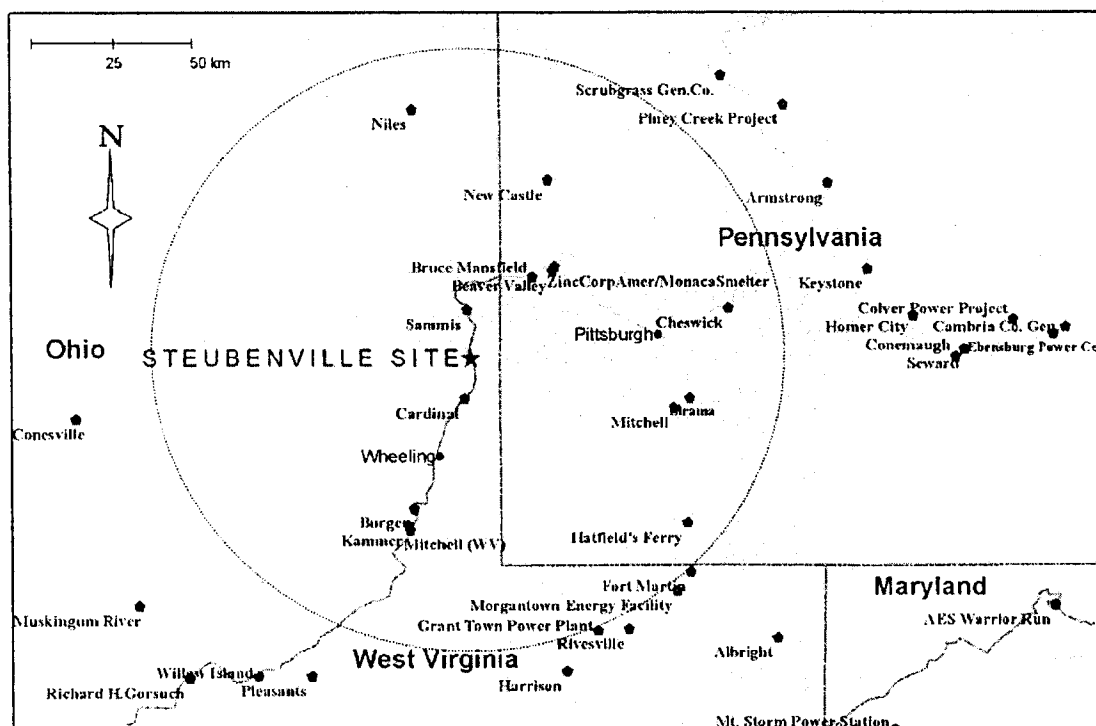


FIGURE 1. Location of the Steubenville, OH monitoring site and surrounding coal-fired utility boilers (circle with 100 km radius centered on site).

developed, improving upon the earlier techniques by using uncertainties in the data matrix (14, 15) as well as through constraining the solutions to non-negative values. Both techniques have the advantage of not requiring prior measurements of source profiles or emission inventories. In this study, PMF and Unmix are applied to the precipitation chemistry data collected at the Steubenville, Ohio site to determine the sources contributing to Hg in wet deposition. In addition, meteorological analysis is performed to provide insights into the probable sources of Hg deposition.

## Methods

**Measurement Site.** An enhanced Hg monitoring site was established in October 2002, in Steubenville, OH on the campus of the Franciscan University (40.379 N, 80.620 W; 306 m above mean sea level) overlooking the Ohio River. This monitoring site was selected because of its proximity to numerous anthropogenic air pollution sources in the Ohio River Valley and because of the human health impacts shown to be caused by these sources during the Harvard Six-City study (16). There are five large coal-fired utility boilers within a 50 km radius of the site and seventeen within 100 km. Figure 1 shows the location of the site as well the location of coal-fired utility boilers in the area.

**Event Deposition Sampling.** Collection of wet deposition on a daily event basis rather than longer duration integrated sampling (e.g., weekly, monthly) is essential for receptor modeling and meteorological analysis (8, 11, 17, 18). The automatic wet-only event precipitation sampling system used for this study is described in detail by Landis and Keeler (19), and has been successfully deployed in the field for more than a decade (8, 20, 21). Precipitation sampling for this study began in October 2002 and will continue through December 2006. Results are reported here for samples collected in CY2003 and CY2004.

For this study, the volume of each precipitation sample was determined gravimetrically, the precipitation depth was

calculated by dividing the precipitation volume by the funnel area, and all events  $\geq 0.1$  cm provided sufficient volume for analysis. A heated tipping-bucket precipitation gauge provided a continuous record of the precipitation received at the site and was used to calculate precipitation depths when the 1 L sample bottles were insufficient for containing the entire event and sample overflow occurred (six events).

All field and analytical supplies used in the collection and analysis of Hg and trace element samples were prepared using an 11-day acid-cleaning procedure (18, 19). The Teflon sample bottles were further prepared by an internal 1% BrCl solution (v/v) soak for a minimum of 24-hours. Standard operating procedures included bottle blank determinations for each batch of cleaned bottles to ensure that sampling bottles were essentially Hg-free before they were deployed into the field (median  $< \text{MDL}$ ;  $5 \pm 14 \text{ pg bottle}^{-1}$  (mean  $\pm$  std dev);  $n = 151$ ).

**Analytical Methods.** Precipitation samples were sent back to the University of Michigan within 24-hours of collection and were processed and analyzed in a Class 100 clean room to avoid potential contamination. Clean room suits and particle-free gloves were worn at all times during preparation and analysis of samples.

**Mercury.** Mercury samples were oxidized with concentrated BrCl to a 1% solution (v/v) and stored in the dark in a cold room for at least 24 h (19). Mercury in precipitation was purged from solution in a Hg-free nitrogen stream after reduction of BrCl with  $\text{NH}_2\text{OH}$  and reduction of divalent Hg by  $\text{SnCl}_2$  to  $\text{Hg}^0$ , and concentrated onto a gold-coated bead trap. Total Hg was then quantified using a dual amalgamation technique followed by cold-vapor atomic fluorescence spectrometry (CVAFS) (19, 22). In a previous study, collocated total Hg samples collected using identical samplers and protocols as those used at Steubenville gave an absolute mean difference in the samples of 8.1% (19). The Method Detection Limit (MDL) for total Hg during this study was determined to be  $0.23 \text{ ng L}^{-1}$ ; determined using EPA method 200.8 (23).

Analytical precision of laboratory replicate Hg analysis during this study was 97.3% ( $n = 51$ ).

**Trace Elements.** Precipitation samples for trace element analysis were acidified with concentrated  $\text{HNO}_3$  to a 0.2% solution (v/v) in the sample bottle and stored in a dark cold room for a minimum of 14 days before analysis to provide adequate time for optimal leaching (24). Precipitation samples were then analyzed for a suite of trace elements using a Finnigan MAT Element magnetic sector field high-resolution inductively coupled plasma mass spectrometer using a method similar to that previously described (25). Trace element isotopes were analyzed in low, medium, or high-resolution depending on the potential of impact of isobaric and/or polyatomic interferences (25). The sensitivity of the element decreases approximately by a factor of 10 with each successive increase in resolution so elements quantified in high-resolution had significantly higher MDLs (See Table S1, Supporting Information).

**Ion Chromatography.** Precipitation samples were analyzed for major anions using a Dionex (Sunnyvale, CA) model DX-600 ion chromatography system equipped with an IonPac AS14 Analytical and AG14 Guard and running a 1.8 mM  $\text{Na}_2\text{CO}_3$ /1.7 mM  $\text{NaHCO}_3$  eluent solution. Precision based on replicate analyses was 95.5 and 93.2%, for nitrate and chloride, respectively.

**Multivariate Statistical Receptor Models.** In this work, two fairly new multivariate receptor modeling approaches were employed: EPA PMF 1.1 (26) and EPA Unmix 5.0 (27). Both PMF and Unmix provide the source compositions, source composition uncertainties, and source contributions to each sample based only on the measured data. These two models use different algorithms and input data with PMF using a combination of concentration and uncertainty data and Unmix using only concentration data. For both models, the sample Hg source contributions were calculated by multiplying the Hg profile value by its source contribution estimate. All samples with sufficient volume from October 2002 through December 2004 were included in the PMF and Unmix analysis ( $n = 162$ ).

EPA PMF couples a graphical user interface with analysis software that implements the PMF 2 model through the multi-linear engine 2 (ME-2), and provides block bootstrap uncertainty estimates (26). All analyses were conducted using the default model specifications, and the results are reported for the run with the lowest Q robust value from 20 random starting points, with random seeds. One hundred bootstrap runs were used to calculate the uncertainty distribution.

EPA Unmix 5.0 includes both a graphical user interface and analysis tools. All analyses were run using the default model specifications and one hundred feasible solutions from a blocked bootstrap were used to calculate the uncertainty distribution (27).

One potential advantage of the PMF model is the ability to weight individual data points using measurement uncertainties and other analytical details such as the elemental MDLs. Here, an objective approach was used to calculate a total deposition uncertainty (U) associated with each data point (each analyte in every sample) for use in PMF by propagating the uncertainty of sample collection (SC), analytical measurement (AM), and precipitation depth (PD) measurement uncertainties (eq 1).

$$U_{\text{Dep}} = \text{MDL} + \sqrt{(\text{SC})^2 + (\text{AM})^2 + (\text{PD})^2} \quad (1)$$

where, MDL = method detection limit; SC = 10%; AM = standard deviation of three replicate analysis; and PD = 5%.

**Meteorological and Trajectory Analysis.** Air mass transport to the Steubenville site was estimated using the hybrid single-particle lagrangian integrated trajectory (HYSPLIT) model version 4.6 (28). HYSPLIT 72-h back trajectories were

**TABLE 1. Volume-weighted Mean (VWM) Hg Concentrations and Total Deposition Calculated from Event Samples Collected Using Identical U of M Samplers in 2003**

site	N	precipitation depth (cm)	VWM Hg (ng L <sup>-1</sup> )	deposition (μg m <sup>-2</sup> y <sup>-1</sup> )
Eagle Harbor, MI <sup>a</sup>	58	64.5	8.3	5.2
Pellston, MI <sup>a</sup>	43	78.7	9.4	7.4
Dexter, MI <sup>a</sup>	60	89.6	11.9	10.7
Steubenville, OH	77	94.8	14.0	13.5

<sup>a</sup> Keeler and Dvonch (21).

calculated using input data from the National Weather Service. The hour of maximum precipitation intensity from each event was used as the start time for the trajectory calculation, and the starting height for each trajectory was calculated as one-half the mixing height, as determined from upper-air soundings. Surface and upper air meteorological maps obtained from the National Weather Service were used to explore the validity of the calculated trajectories and to better understand the type of precipitation and meteorological patterns that influenced the deposition events.

## Results and Discussion

**Concentrations and Deposition.** The 2-year record of Hg in event precipitation at Steubenville is the only such record collected in Ohio to date. The volume-weighted mean (VWM) Hg concentration was 13.7 ng L<sup>-1</sup> for the 2-year period, with little difference between the years (14.0 and 13.5 ng L<sup>-1</sup> for 2003 and 2004, respectively). The range in the event Hg concentrations recorded over the 2-year period in Steubenville was 4.0–78.9 ng L<sup>-1</sup>, similar to the range of Hg concentrations observed in a highly industrialized area in southeast Michigan during the same time period (21). However, the distribution of the Hg concentrations observed in Steubenville was quite different than those measured at rural sites in Michigan and Vermont using identical samplers (20, 21). The minimum or baseline Hg concentration observed at Steubenville was ~4 ng L<sup>-1</sup>; about 4 times higher than the baseline concentrations recorded during the same period at rural sites in Michigan and at Underhill, VT.

The Hg wet deposition recorded at the Steubenville site was 13.5 and 19.7 μg m<sup>-2</sup> y<sup>-1</sup> in 2003 and 2004, respectively. Table 1 shows a comparison of the 2003 VWM concentrations and the annual deposition reported for three sites in Michigan with that at Steubenville (21). The Hg wet deposition observed at Steubenville in 2003 was ~25% greater than that received at Dexter, MI and ~2.5 times that recorded at the northern most site located in Eagle Harbor, MI. The pattern observed in 2003, with a south to north Hg deposition gradient across Michigan, has been observed consistently over the past decade through collection of event precipitation samples at several sites in Michigan (8, 18, 21). The higher Hg deposition observed at the Steubenville site was not unexpected, because of the density of Hg sources in the upwind region such as coal-fired utility boilers, iron-steel manufacturing, incinerators, and other non-ferrous metal processing industries (9). The Hg deposition recorded at the Steubenville site in 2004 was 19.7 μg m<sup>-2</sup> year<sup>-1</sup>, 46% greater than the previous year. The VWM concentrations for the 2003–2004 period for the trace elements used for source apportionment are provided in the Supporting Information (Table S1).

**PMF Model Results.** PMF solutions with six and seven sources were evaluated, and species contributions to sources were considered significant if the fifth percentile of the bootstrap uncertainty distribution was greater than 0. The results from the six-source solution are presented based on

TABLE 2. PMF Source Profiles for Steubenville Event Precipitation Data<sup>a</sup>

analyte	source 1 iron/steel production	source 2 oil and incineration	source 3 crustal	source 4 coal combustion	source 5 phosphorous	source 6 molybdenum
Mg	187	*	558	*	101	*
Al	51	80	355	37	*	52
P	7.8	*	*	*	63.8	*
S	*	*	642	11299	197	*
Cl	267	20480	*	584	*	771
V	2.9	1.1	*	*	*	*
Cr	2.5	*	*	*	*	*
Mn	54.4	*	34.1	*	15.4	*
Fe	344	102	17	37	27	*
Ni	*	3.19	*	*	0.68	*
Cu	1.8	14.0	*	18.4	2.7	7.0
Zn	4.0	44.1	6.1	10.7	5.3	15.6
As	*	0.81	0.10	0.49	0.05	0.27
Se	*	0.97	*	1.73	*	1.30
Rb	*	0.25	0.15	0.20	0.29	0.08
Sr	0.48	3.30	5.64	0.95	1.61	*
Mo	*	*	*	*	*	4.02
Cd	0.09	0.27	*	0.31	0.02	0.23
La	*	0.13	0.63	*	*	0.04
Ce	0.02	*	1.23	*	*	*
Hg	0.01	*	*	0.15	< 0.01	*
Pb	1.10	6.59	0.59	3.62	0.36	1.13
NO <sub>3</sub> <sup>-</sup>	*	8639	1501	4532	314	*
% Hg	6	*	*	73	2	*

\* means not significant at 95% confidence interval.

the ability to identify the sources and the bootstrap uncertainty results. The six-source solution was composed of iron/steel production (V, Cr, Mn, Fe), oil and incineration (V, Ni, Zn, Cd, Pb), crustal (Mg, Al, Sr, La, Ce), coal combustion (S, Se, NO<sub>3</sub><sup>-</sup>), phosphorus (P, Mg, Mn, Fe, Sr), and molybdenum (Mo, Cu). The seven-source solution separated out one additional crustal source (La, Ce, Mg), and the Hg contributions from coal for the six- and seven-source solutions were similar with 73 and 70%, respectively. Three sources contributed significant amounts of Hg: iron/steel production (6%), coal combustion (73%), and phosphorus (2%). The results determined from the six-source solution are presented in Table 2.

While PMF was able to separate out six sources, the source identified as coal combustion was clearly dominant in terms of explaining the Hg deposition. Atmospheric Se is often associated with the burning of fossil fuels such as coal (29, 30), and Se in the absence of significant Ni and V was determined to be an appropriate tracer of coal combustion in Steubenville (31). There are several large steel manufacturing facilities in the Steubenville, OH–Wheeling, WV area as well as plants to the east in Pittsburgh, and iron-steel production was found to be a minor contributor to Hg deposition in this study. An unidentified phosphorus source was also found to be significant small contributors to Hg deposition. The elements Zn, Pb, Cu, and Cl have been used to identify municipal waste incinerator emissions (11, 32), and the elements Ni and V are commonly used tracers to identify oil combustion (33, 34). Two other sources of trace elements were identified in the event deposition data using PMF: a crustal source (24, 35) and a molybdenum source. The molybdenum source may be production of Mo which is used in the steel industry. However, neither was found to be a significant contributor to Hg wet deposition during the study period.

The model (sum of the calculated source contributions) does an excellent job of reproducing the observations except for several of the top deposition events over the 2 years of record. The regression results of the PMF predicted versus measured Hg had a slope of 0.70, an intercept of 0.05, and a coefficient of determination of 0.85 ( $n = 162$ ). Figure 2a

depicts the time series of the predicted deposition from coal combustion versus observed Hg wet deposition at Steubenville using the PMF six-source model solution, showing the clearly dominant impact of coal combustion.

**Unmix Results.** Unmix identified one influential Ni data point and its value was replaced using the missing data algorithm (Ni on 04-07-2003, measured = 364.15 ng m<sup>-2</sup>, replaced = 8.44 ng m<sup>-2</sup>). A reduced number of species was used in the Unmix run: Hg, Cd, La, Ce, Mg, Al, P, S, V, Cr, Mn, Fe, Ni, Se, and NO<sub>3</sub><sup>-</sup> because using less species improved the stability of the uncertainty estimate. The source profiles for a feasible six source solution produced by Unmix are given in Table 3, and species contributions to each source were considered significant if the fifth percentile of the bootstrap uncertainty distribution was greater than 0. Identification of the sources was performed in a similar way to that with the PMF solutions. The Unmix model found six sources which were identified as phosphorus, incinerator, nickel, iron/steel production, crustal, and coal combustion sources. Only three sources contributed significant amounts of Hg including incinerator (12%), nickel (12%), and coal combustion (69%). The regression results of the Unmix predicted versus measured Hg had a slope of 1.00, an intercept of -0.02, and a coefficient of determination of 0.86 ( $n = 162$ ).

**Comparison of Unmix and PMF.** Both models tracked the measured values closely but under-predicted the peak depositions. Two high deposition Hg events occurred on 08/29/2004 (1.53  $\mu\text{g m}^{-2}$ ) and 09/08/2004 (1.69  $\mu\text{g m}^{-2}$ ) shown in Figures 2a and b as events 146 and 147 in the time series. The Unmix and PMF Hg results for these two events were 1.08 and 1.40  $\mu\text{g m}^{-2}$ , and 0.85 and 1.08  $\mu\text{g m}^{-2}$  respectively. Table 4 shows that Unmix over-predicted the total measured Hg deposition by 13 and 5%, while PMF under-predicted by 7 and 11% in 2003 and 2004, respectively.

Confidence intervals (CI) were calculated for those sources identified by Unmix and PMF as a measure of the uncertainty associated with their contribution to Hg deposition. The 95% confidence interval (CI) was calculated using the fifth and 95th percentiles of the source profile uncertainty distributions. Total coal Hg contributions were 23.7  $\mu\text{g m}^{-2}$ , with a CI of 16.7–38.4  $\mu\text{g m}^{-2}$  for PMF, and 26.8  $\mu\text{g m}^{-2}$ , with a CI

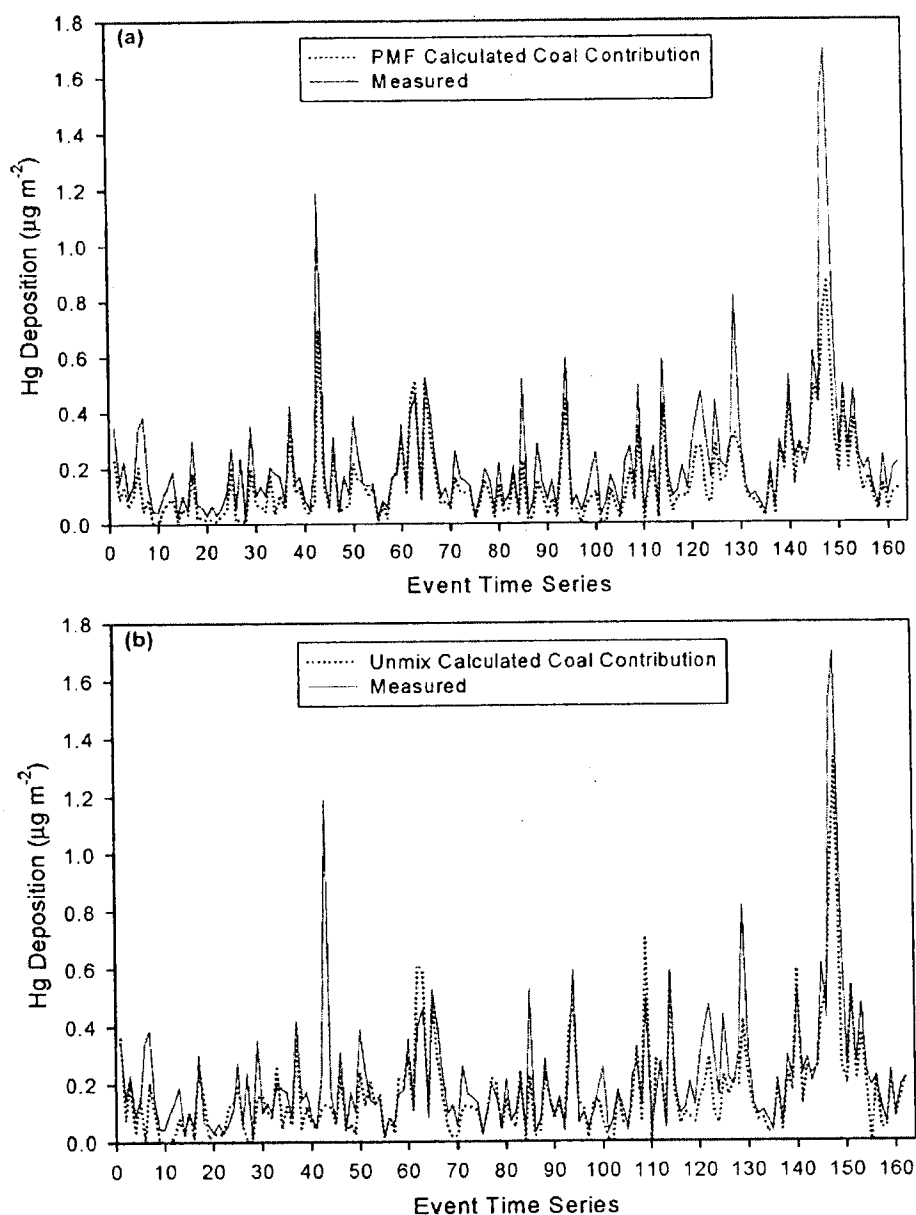


FIGURE 2. (a) PMF predicted deposition from coal combustion versus measured deposition of Hg at Steubenville, OH (2003–2004). (2b) Unmix predicted deposition from coal combustion versus measured deposition of Hg at Steubenville, OH (2003–2004).

of  $16.4\text{--}39.1\text{ }\mu\text{g m}^{-2}$  for Unmix during the study period. Two additional PMF sources had significant Hg contributions: phosphorus total of  $0.6\text{ }\mu\text{g m}^{-2}$  with a CI  $0.3\text{--}1.5\text{ }\mu\text{g m}^{-2}$ , iron/steel production total of  $1.9\text{ }\mu\text{g m}^{-2}$  with a CI  $0.1\text{--}3.4\text{ }\mu\text{g m}^{-2}$ . Unmix also had two additional sources with significant Hg contributions: incinerator total of  $4.6\text{ }\mu\text{g m}^{-2}$  with a CI  $0.1\text{--}10.2$ ; and nickel total of  $4.5\text{ }\mu\text{g m}^{-2}$  with a CI  $0.4\text{--}7.1$ . The lack of agreement between Unmix and PMF for these small Hg sources may indicate that these sources contribute too little to be accurately quantified. Average results from both PMF and Unmix are well within the confidence intervals stated for both model estimates, and this wide range of uncertainties will be reduced as additional samples are included in the analysis at the conclusion of this study (CY2006).

As clearly stated in Poirot et al. (35), receptor models, such as PMF and Unmix, start with the assumption that the source compositions are constant and unique, and that source contributions vary over time. These assumptions may not be well met when attempting to apportion sources that emit species that undergo atmospheric transformations and form secondary species such as sulfate aerosols. Mercury chemistry may be even more complicated than that of sulfur as a larger fraction of the emissions are emitted in the oxidized forms that deposits more quickly than the  $\text{Hg}^0$  form that is emitted concurrently. While this limitation is also acknowledged here, the use of multiple receptor models together with the meteorological analysis provided below offer independently consistent results and findings.

TABLE 3. Unmix Source Profiles for Steubenville Precipitation Data<sup>a</sup>

analyte	source 1 phosphorous	source 2 incinerator	source 3 Ni	source 4 iron/steel production	source 5 crustal	source 6 coal combustion
Mg	103	*	*	120	869	*
Al	*	*	37	*	482	*
P	73.0	*	*	5.4	*	*
S	*	1069	1754	*	*	10494
V	*	*	0.85	3.16	*	1.35
Cr	*	*	*	3.2	*	0.4
Mn	18.5	*	*	50.9	50.3	*
Fe	33	*	55	356	70	93
Ni	*	*	11.75	0.74	*	*
Se	*	*	*	0.87	*	4.26
Cd	*	0.93	0.08	*	*	0.23
La	*	*	0.07	*	0.76	*
Ce	*	*	0.15	*	1.44	*
Hg	*	0.03	0.03	*	*	0.16
NO <sub>3</sub>	*	*	*	*	1860	7518
% Hg	*	12	12	*	*	69

\* means not significant at 95% confidence interval

TABLE 4. Comparison of Measured Total Hg Wet Deposition ( $\mu\text{g m}^{-2}$ ) at Steubenville, OH Site to PMF and Unmix Coal Combustion Contribution Estimates

year	total measured Hg wet deposition	PMF estimated Hg		Unmix estimated Hg	
		coal	total	coal	total
2003	13.5	9.1	12.2	9.9	14.8
2004	19.7	13.1	17.6	15.5	21.1

#### Climatology, Meteorology, and Sample Variability.

Investigations using relatively short meteorological records, e.g., 2-years, need to place the shorter record into a larger climatologically relevant context. While significant differences in the Steubenville wind speed and direction were not expected nor observed, for the CY2003–2004 period from the long-term norm, differences in temperature and precipitation were thought to be more likely. In fact, while the CY 2003 rainfall total was representative of the Steubenville climatological norm, significantly more rain than normal fell in CY 2004, with 10 of 12 months above average and the majority of the excess rainfall occurring in September. CY 2003 was a unique year for eastern Ohio in terms of frozen precipitation; snowfall totals were well over twice the climatologically expected amount. These facts help explain the large deviation between the annual deposition totals (13.5 and 19.7  $\text{g m}^{-2}$ ) despite annual VWA Hg concentration similarities, because snow in temperate latitudes appears to be much less efficient at capturing Hg via wet deposition (8). In addition, the long-term study of event precipitation collected in Vermont over 11-years found average surface temperatures were highly correlated with the monthly total deposition at that site (20). However, the average surface temperatures for CY 2003 and 2004, did not significantly deviate from the climatological norm.

Individual precipitation events can contribute significantly to the annual Hg deposition total at individual sites (20, 21). This was clearly seen in the Steubenville record as the top five Hg deposition events (1.69, 1.53, 1.19, 0.82, and 0.77  $\mu\text{g m}^{-2}$  seen in Figures 2a and b as events 147, 146, 42, 128, and 148, respectively) all had above average Hg concentrations as well as precipitation depths. While one of these (sample 43) contained precipitation from more than one distinct event and, therefore, cannot be clearly categorized meteorologically, the other four samples corresponded to discrete summer-time events. Two of the discrete events were associated with remnants of September hurricanes (Frances

and Ivan; samples 147 and 148), one was associated with a warm sector squall line (sample 47) and the fourth (sample 148) occurred in a series of intense precipitation events associated with outflow boundary cells preceding a stationary front. The origin of feed air for these types of precipitating systems is fairly unique; the vertical structure of a strong mid-latitude cyclone dynamically allows exceptional local entrainment and wet deposition, cleaning out the atmospheric boundary layer as the storm sweeps through. Sample 128 was associated with a squall line that formed in the warm sector of a low-pressure system only hours before it reached Steubenville, indicating that the entrained air was from within a relatively short distance of the site, as outflow boundaries force lift and condensation on a local scale. Surface winds associated with the two hurricane events were primarily from the northeast, while the other events experienced weak surface winds primarily from the south–southwest which are both areas that contain a high density of coal-fired utility boilers. Three-day back trajectories also indicated air masses with origins northeast or south–southwest of the Steubenville site for these four events (See Figures S3a–e, Supporting Information). The observation of local stagnation prior to large Hg deposition events in Steubenville was also observed at a site in Chicago, IL during the Lake Michigan Mass Balance Study (8). Weak surface winds prior to the precipitation events in Chicago lead to higher observed Hg deposition at that site, but at rural sites in South Haven and Sleeping Bear Dunes, MI, local stagnation did not lead to elevated deposition. At these rural sites, the highest Hg concentrations and wet deposition, were observed after relatively fast transport from the Chicago/Gary area.

The average rainfall rates for these high deposition events were approximately three times the 2-year average (5.7 and 1.7  $\text{mm h}^{-1}$ , respectively) and four of the top five events had maximum rainfall occurring in late night/early morning hours when the boundary layer is relatively shallow. Maximum rainfall times for the 2-year period did not, on average, show a preference to any particular time of day.

The influence of local and regional sources is also evident when comparing the Hg concentrations of event samples collected at different sites following the path of hurricane Frances, Steubenville's highest deposition event of the 2-year record. The center of the low for this system moved northward into the Mid-Atlantic states and then toward the northeast, while winds prior to and during the precipitation period at Steubenville were out of the northeast. The Hg concentration at Steubenville for this event was 18.7  $\text{ng L}^{-1}$ , the concentration found in samples with similar volume collected during

Hurricane Frances at a site in Underhill, Vermont was less than half that at Steubenville ( $9.1 \text{ ng L}^{-1}$ ) and that collected at a site in Tampa where the feed air was primarily of oceanic origin was  $4.1 \text{ ng L}^{-1}$ .

The large temporal variability and range of concentrations among the event samples in Steubenville during this study ( $4.0\text{--}78.9 \text{ ng L}^{-1}$ ) also indicates a strong local and regional source influence. Only 9.5% of the variability in concentration could be accounted for by precipitation amount alone. In addition, a large range was found in Hg concentrations among samples with a similar precipitation depth:  $4.3\text{--}78.9 \text{ ng L}^{-1}$  for low precipitation depth samples ( $<1 \text{ cm}$ ) and  $4.2\text{--}22.1 \text{ ng L}^{-1}$  for high precipitation depth samples ( $>5 \text{ cm}$ ). Previous studies have shown that a large range in concentration for similar rainfall amounts can be attributed to variability in impacts by local sources and to the variation in distance between the sources and the receptor site (8, 36, 37).

The results of the multivariate statistical analysis ( $\sim 70\%$  of the Hg in the wet deposition at Steubenville coal combustion sources), and meteorological analysis (highlighting the importance of local regional sources), consistently point toward the dominant influence by local and regional coal-burning sources.

### Acknowledgments

The United States Environmental Protection Agency through its Office of Research and Development funded the research described here through cooperative agreement R-82971601 with the University of Michigan. It has been subjected to Agency review and approved for publication. We thank Jim Barres and Ali Kamal (UMAQL) for managing laboratory support operations and data processing; Minghao Zhou and Julie Peterson for the precipitation analysis; Dr. Khalid Al-Wali for trajectory calculation and plotting; Dr. Frank Marsik for meteorological measurements and interpretation; Dr. James Slater (Franciscan University) for on-site logistical support; and Dr. Ron Henry (USC) and Shelly Eberly (EPA) for receptor modeling support. We also thank the reviewers for their insightful comments and suggestions.

### Supporting Information Available

MDLs and volume-weighted mean concentrations for all of the trace elements in Table S1. Scatter plots of PMF and Unmix modeled versus observed Hg deposition in Figures S2a-b. Three day back trajectory plots for high deposition events in Figures S3a-d. This material is available free of charge via the Internet at <http://pubs.acs.org>.

### Literature Cited

- Landis, M. S.; Keeler, G. J. Atmospheric mercury deposition to Lake Michigan during the Lake Michigan mass balance study. *Environ. Sci. Technol.* **2002**, *36*, 4518–4524.
- Rolfhus, K. R.; Sakamoto, H. E.; Cleckner, L. B.; Stoor, R. W.; Babiartz, C. L.; Back, R. C.; Manolopoulos, H.; Hurley, J. P. Distribution and fluxes of total and methylmercury in Lake Superior. *Environ. Sci. Technol.* **2003**, *37*, 865–872.
- Nriagu, J. Global metal pollution: poisoning the biosphere. *Environment* **1990**, *32*, 28–32.
- EPMAF. *Mercury Atmospheric Processes: A Synthesis Report*. EPRI/TR-104214; Expert Panel on Mercury Atmospheric Processes: Palo Alto, CA, 1994.
- Keeler, G.; Glinson, G.; Pirrone, N. Particulate mercury in the atmosphere: its significance, transport, transformation and sources. *Water Air Soil Pollut.* **1995**, *80*, 159–168.
- Landis, M. S.; Keeler, G. J.; Al-Wali, K. I.; Stevens, R. K. Divalent inorganic reactive gaseous mercury emissions from a mercury cell chlor-alkali plant and its impact on near-field atmospheric dry deposition. *Atmos. Environ.* **2004**, *38*, 613–622.
- Iverfeldt, A. Occurrence and turnover of atmospheric mercury over the Nordic countries. *Water, Air, Soil Pollut.* **1991**, *56*, 251–265.
- Landis, M. S.; Vette, A. F.; Keeler, G. J. Atmospheric Mercury in the Lake Michigan Basin: Influence of the Chicago/Gary Urban Area. *Environ. Sci. Technol.* **2002**, *36*, 4508–4517.
- U.S. Environmental Protection Agency. *Mercury Study Report to Congress*, EPA-452/R-97-005; Office of Air Quality Planning and Standards, Office of Research and Development: Washington, DC, 1997.
- U.S. Environmental Protection Agency. Standards of performance for new and existing stationary sources: Electric utility steam generating units; Final Rule. *Fed. Regist.* **2005**, *70*, 95.
- Dvonch, J. T.; Graney, J. R.; Keeler, G. J.; Stevens, R. K. Use of elemental tracers to source apportion mercury in south Florida precipitation. *Environ. Sci. Technol.* **1999**, *33*, 4522–4527.
- Anderson, M. J.; Daly, E. P.; Miller, S. L.; Milford, J. B. Source apportionment of exposures to volatile organic compounds. I. Evaluation of receptor models using simulated exposure data. *Atmos. Environ.* **2002**, *36*, 3643–3658.
- Lewis, C. W.; Norris, G.; Henry, R. Source apportionment of Phoenix PM<sub>2.5</sub> aerosol with the Unmix receptor model. *J. Air Waste Manage. Assoc.* **2003**, *53*, 325–338.
- Paatero, P.; Tapper, U. Positive matrix factorization—a non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* **1994**, *5*, 111–126.
- Anttila, P.; Paatero, P.; Tapper, U.; Jarvinen, O. Source identification of bulk wet deposition in Finland by positive matrix factorization. *Atmos. Environ.* **1995**, *14*, 1705–1718.
- Dockery, D. W.; Pope, C.; Xu, X.; Spengler, J.; Ware, J.; Fay, M.; Ferris, B.; Speizer, F. An association between air pollution and mortality in six U.S. cities. *N. Engl. J. Med.* **1993**, *329*, 1753–1759.
- Ross, H. B. Trace metal wet deposition in Sweden: insight gained from daily wet only collection. *Atmos. Environ.* **1990**, *24A*, 1929.
- Hoyer, M. E.; Burke, J. B.; Keeler, G. J. Atmospheric sources, transport and deposition of mercury in Michigan: two years of event precipitation. *Water, Air, Soil Pollut.* **1995**, *80*, 199–208.
- Landis, M. S.; Keeler, G. J. Critical evaluation of a modified automatic wet-only precipitation collector for mercury and trace element determinations. *Environ. Sci. Technol.* **1997**, *31*, 2610–2615.
- Keeler, G. J.; Gratz, L.; Al-Wali, K. Influences on the long-term atmospheric mercury wet deposition at Underhill, Vermont. *Ecotoxicology* **2005**, *14*, 71–83.
- Keeler, G. J.; Dvonch, J. T. Atmospheric mercury: A decade of observations in the Great Lakes. In *Dynamics of Mercury Pollution on Regional and Global Scales: Atmospheric Processes and Human Exposures around the World*; Pirrone, N., Mahaffey, K., Eds.; Kluwer Ltd: Norwell, MA, 2005.
- Fitzgerald, W. F.; Gill, G. A. Subnanogram determination of mercury by two-stage gold amalgamation and gas phase detection applied to atmospheric analysis. *Anal. Chem.* **1979**, *51*, 1714–1720.
- U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory. *Methods for the Determination of Metals in Environmental Samples*; CRC Press: Boca Raton, FL, 1992; pp 95–137.
- Graney, J. R.; Landis, M. S.; Norris, G. A. Concentrations and solubilities of metals from indoor and personal exposure PM<sub>2.5</sub> samples. *Atmos. Environ.* **2004**, *38*, 237–247.
- Montaser, A. *Inductively Coupled Plasma Mass Spectrometry*; Wiley-VCH Inc.: New York, 1998.
- Eberly, S. *EPA PMF 1.1 User's Guide*, U.S. Environmental Protection Agency: Washington, DC, 2005.
- Norris, G.; Henry, R.; Vedantham, R. *EPA Unmix 5.0 User Guide*, U.S. Environmental Protection Agency: Washington, DC, 2006.
- Draxler, R. R.; Hess, G. D. *Description of the HYSPLIT\_4 Modeling System*. NOAA Technical Memorandum ERL ARL-224; NOAA: Washington, DC, 1997.
- Biegalski, S. R.; Landsberger, S.; Hoff, R. M. Source-receptor modeling using trace metals in aerosols collected at three rural Canadian Great Lakes sampling stations. *J. Air Waste Manage. Assoc.* **1998**, *48*, p227.
- Gordon, G. E. Receptor models. *Environ. Sci. Technol.* **1988**, *22*, 1132–1142.
- Grahame, T.; Hidy, G. Using factor analysis to attribute health impacts of particulate pollution sources. *Inhalation Toxicol.* **2004**, *16*, 143–152.
- Greenberg, R. R.; Gordon, G. E.; Zoller, W. H.; Jacko, R. B.; Neuendorf, D. W.; York, K. J. Composition of particles emitted from the Nicosia municipal incinerator. *Environ. Sci. Technol.* **1978**, *12*, 1329–1332.

- (33) Kitto, M. E. Trace-element patterns in fuel oils and gasolines for use in source apportionment. *J. Air Waste Manage. Assoc.* **1993**, *43*, 1381–1388.
- (34) Suarez, A. E.; Ondov, J. M. Ambient aerosol concentrations of elements resolved by size and by source: contributions of some cytotoxic-active metals from coal- and oil-fired power plants. *Energy Fuels* **2002**, *16*, 562–568.
- (35) Poirot, R. L.; Wishinski, P. R.; Hopke, P. K.; Polissar, A. V. Comparative application of multiple receptor methods to identify aerosol sources in northern Vermont. *Environ. Sci. Technol.* **2001**, *35*, 4622–4636.
- (36) Moody, J. L.; Samson, P. J. The influence of atmospheric transport on precipitation chemistry at two sites in the Midwestern United States. *Atmos. Environ.* **1989**, *23*, 2117–2132.
- (37) Dvonch, J. T.; Keeler, G. J.; Marsik, F. J. The influence of meteorological conditions on the wet deposition of mercury in southern Florida. *J. Appl. Meteor.* **2005**, *44*, 1421–1435.

Received for review February 16, 2006. Revised manuscript received July 13, 2006. Accepted July 28, 2006.

ES060377Q

# **Modeling the Fate and Transport of Atmospheric Mercury in the Chesapeake Bay Region**



**Dr. Mark Cohen  
NOAA Air Resources Laboratory  
Silver Spring, Maryland**



**Presentation at  
NOAA Chesapeake Bay Office  
May 17, 2004, Annapolis MD**



- **Modeling Methodology**
- **Hg Emissions Inventory**
- **Model Evaluation**
- **Some Results for Chesapeake Bay**
- **Some Next Steps**

# **Modeling Methodology**

# Three “forms” of atmospheric mercury



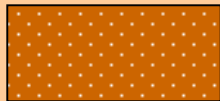
## Elemental Mercury: Hg(0)

- ~ 95% of total Hg in atmosphere
- *not* very water soluble
- long atmospheric lifetime (~ 0.5 - 1 yr); globally distributed



## Reactive Gaseous Mercury (“RGM”)

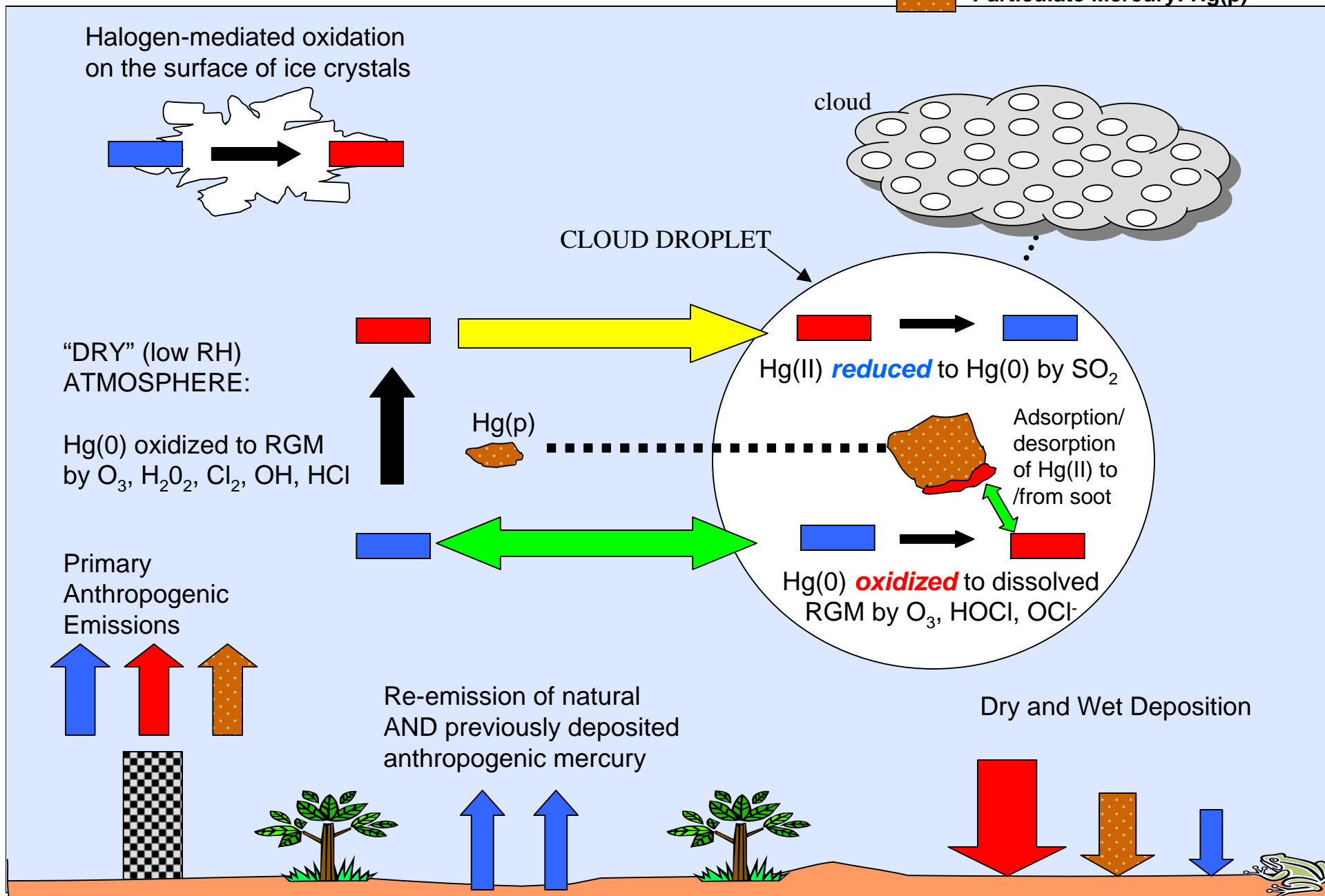
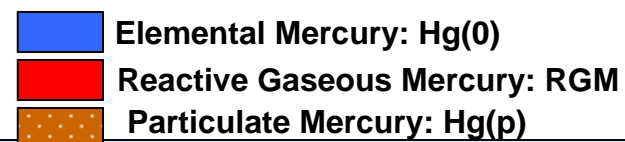
- a few percent of total Hg in atmosphere
- oxidized mercury: Hg(II)
- HgCl<sub>2</sub>, others species?
- somewhat operationally defined by measurement method
- *very* water soluble
- short atmospheric lifetime (~ 1 week or less);
- more local and regional effects



## Particulate Mercury (Hg(p))

- a few percent of total Hg in atmosphere
- not pure particles of mercury...  
(Hg compounds associated with atmospheric particulate)
- species largely unknown (in some cases, may be HgO?)
- moderate atmospheric lifetime (perhaps 1~ 2 weeks)
- local and regional effects
- bioavailability?

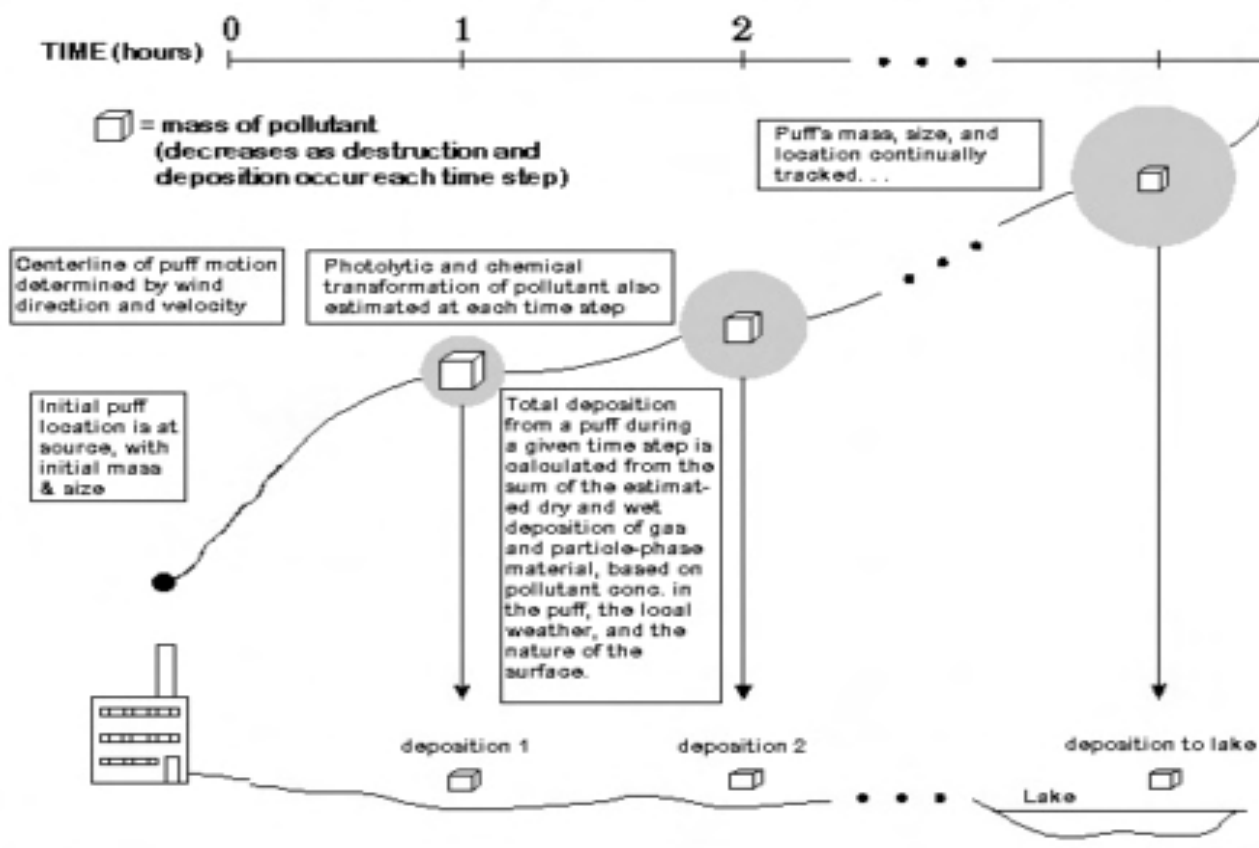
# Atmospheric Fate Processes for Hg



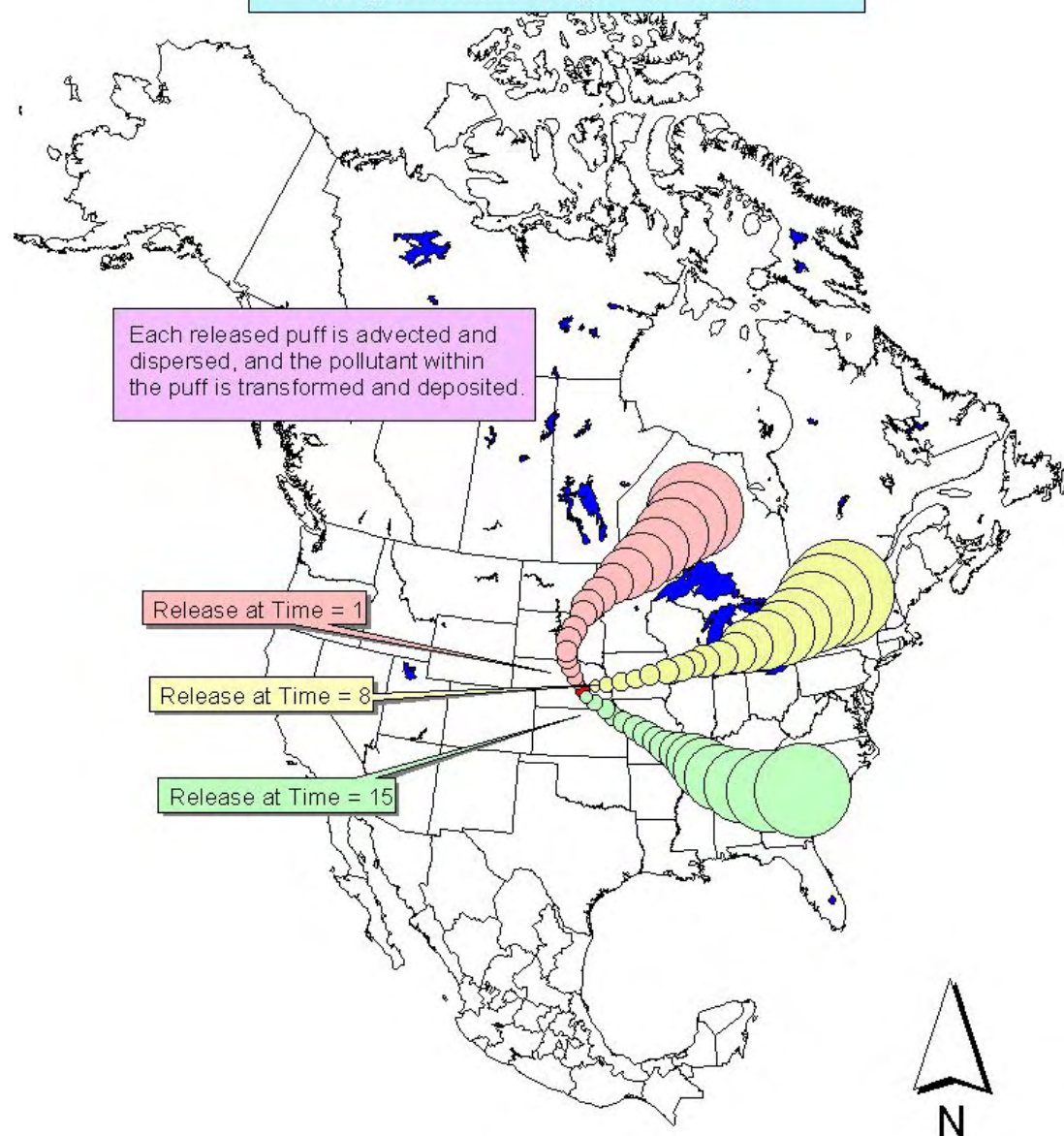
# Atmospheric Chemical Reaction Scheme for Mercury

Reaction	Rate	Units	Reference
<b><i>GAS PHASE REACTIONS</i></b>			
$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg(p)}$	3.0E-20	cm <sup>3</sup> /molec-sec	Hall (1995)
$\text{Hg}^0 + \text{HCl} \rightarrow \text{HgCl}_2$	1.0E-19	cm <sup>3</sup> /molec-sec	Hall and Bloom (1993)
$\text{Hg}^0 + \text{H}_2\text{O}_2 \rightarrow \text{Hg(p)}$	8.5E-19	cm <sup>3</sup> /molec-sec	Tokos et al. (1998) (upper limit based on experiments)
$\text{Hg}^0 + \text{Cl}_2 \rightarrow \text{HgCl}_2$	4.0E-18	cm <sup>3</sup> /molec-sec	Calhoun and Prestbo (2001)
$\text{Hg}^0 + \text{OH} \rightarrow \text{Hg(p)}$	8.7E-14	cm <sup>3</sup> /molec-sec	Sommar et al. (2001)
<b><i>AQUEOUS PHASE REACTIONS</i></b>			
$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg}^{+2}$	4.7E+7	(molar-sec) <sup>-1</sup>	Munthe (1992)
$\text{Hg}^0 + \text{OH} \rightarrow \text{Hg}^{+2}$	2.0E+9	(molar-sec) <sup>-1</sup>	Lin and Pehkonen(1997)
$\text{HgSO}_3 \rightarrow \text{Hg}^0$	$T * e^{((31.971 * T) - 12595.0) / T} \text{ sec}^{-1}$ [T = temperature (K)]		Van Loon et al. (2002)
$\text{Hg(II)} + \text{HO}_2 \rightarrow \text{Hg}^0$	~ 0	(molar-sec) <sup>-1</sup>	Gardfeldt & Jonnson (2003)
$\text{Hg}^0 + \text{HOCl} \rightarrow \text{Hg}^{+2}$	2.1E+6	(molar-sec) <sup>-1</sup>	Lin and Pehkonen(1998)
$\text{Hg}^0 + \text{OCl}^{-1} \rightarrow \text{Hg}^{+2}$	2.0E+6	(molar-sec) <sup>-1</sup>	Lin and Pehkonen(1998)
$\text{Hg(II)} \leftrightarrow \text{Hg(II)}_{(\text{soot})}$	9.0E+2	liters/gram; t = 1/hour	eqnbrm: Seigneur et al. (1998) rate: Bullock & Brehme (2002).
$\text{Hg}^{+2} + \text{h} \rightarrow \text{Hg}^0$	6.0E-7	(sec) <sup>-1</sup> (maximum)	Xiao et al. (1994); Bullock and Brehme (2002)

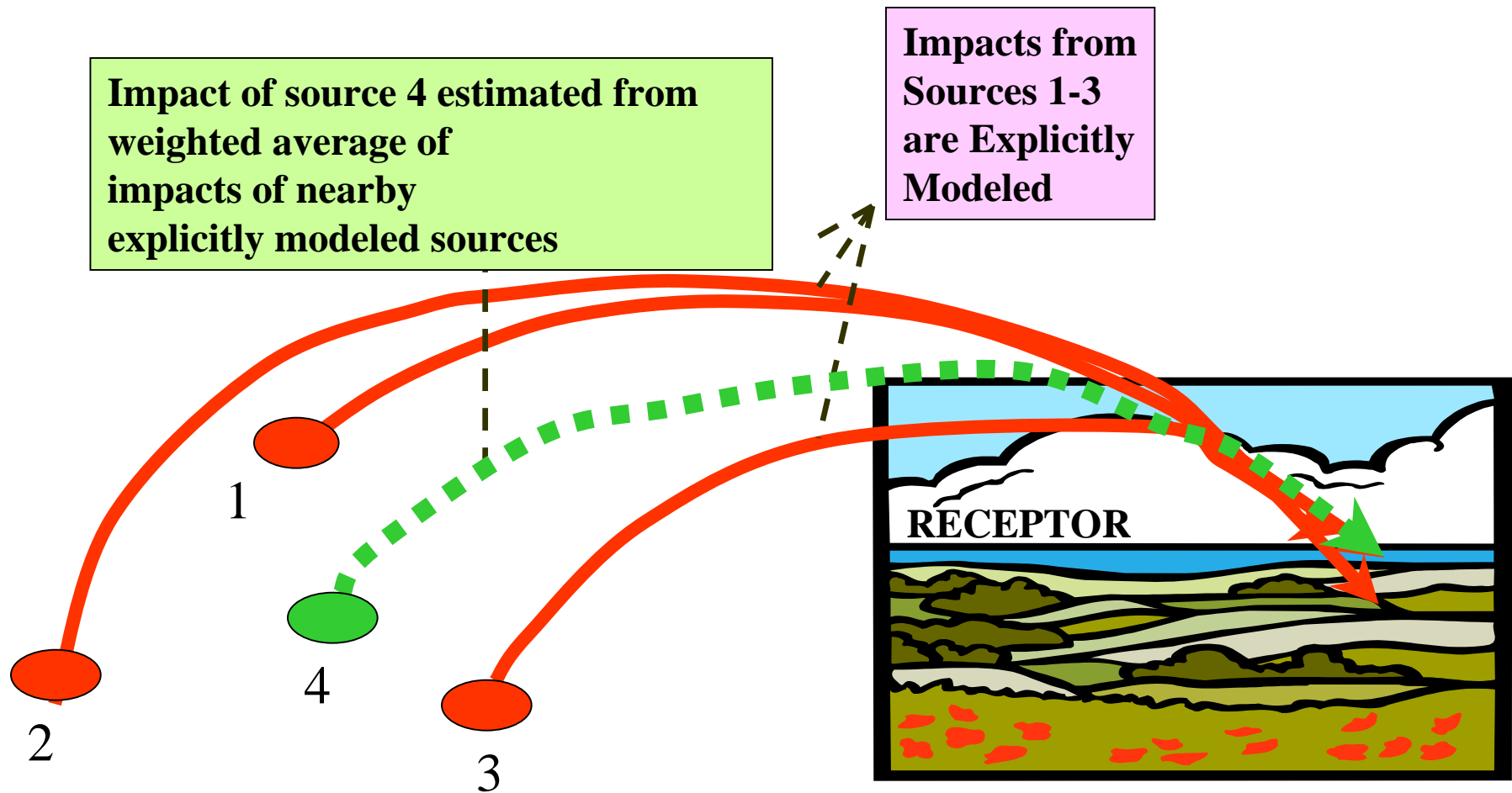
Figure 1. Lagrangian Puff Air Transport and Deposition Model



Over the entire modeling period  
(e.g., one year), puffs are released  
at periodic intervals  
(e.g., once every 7 hours).



# Spatial interpolation

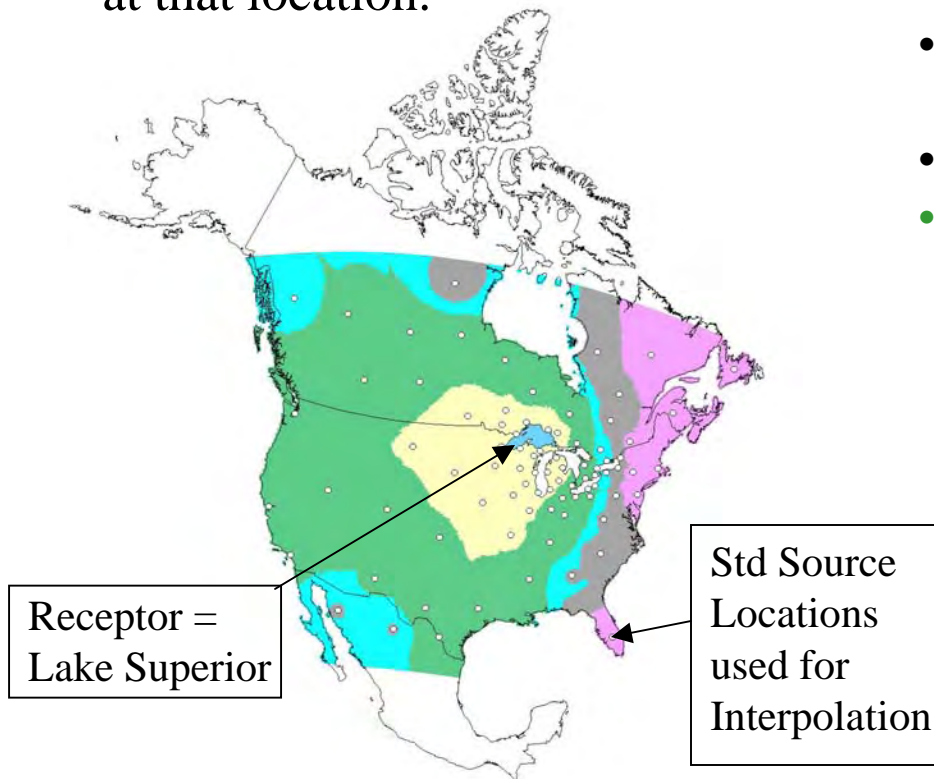




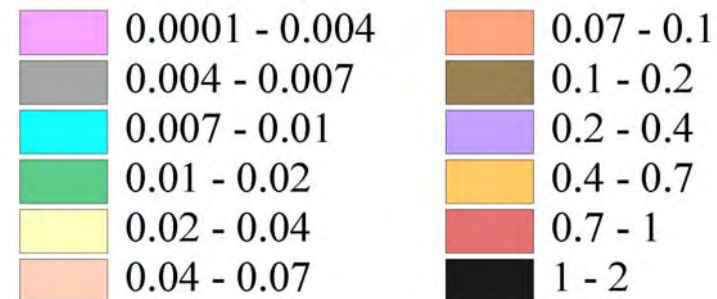
at any given location,  
the **transfer coefficient**  
is defined as the amount  
that would be deposited  
in the given receptor  
(in this case, Lake Superior)  
**if** there were emissions  
at that location.

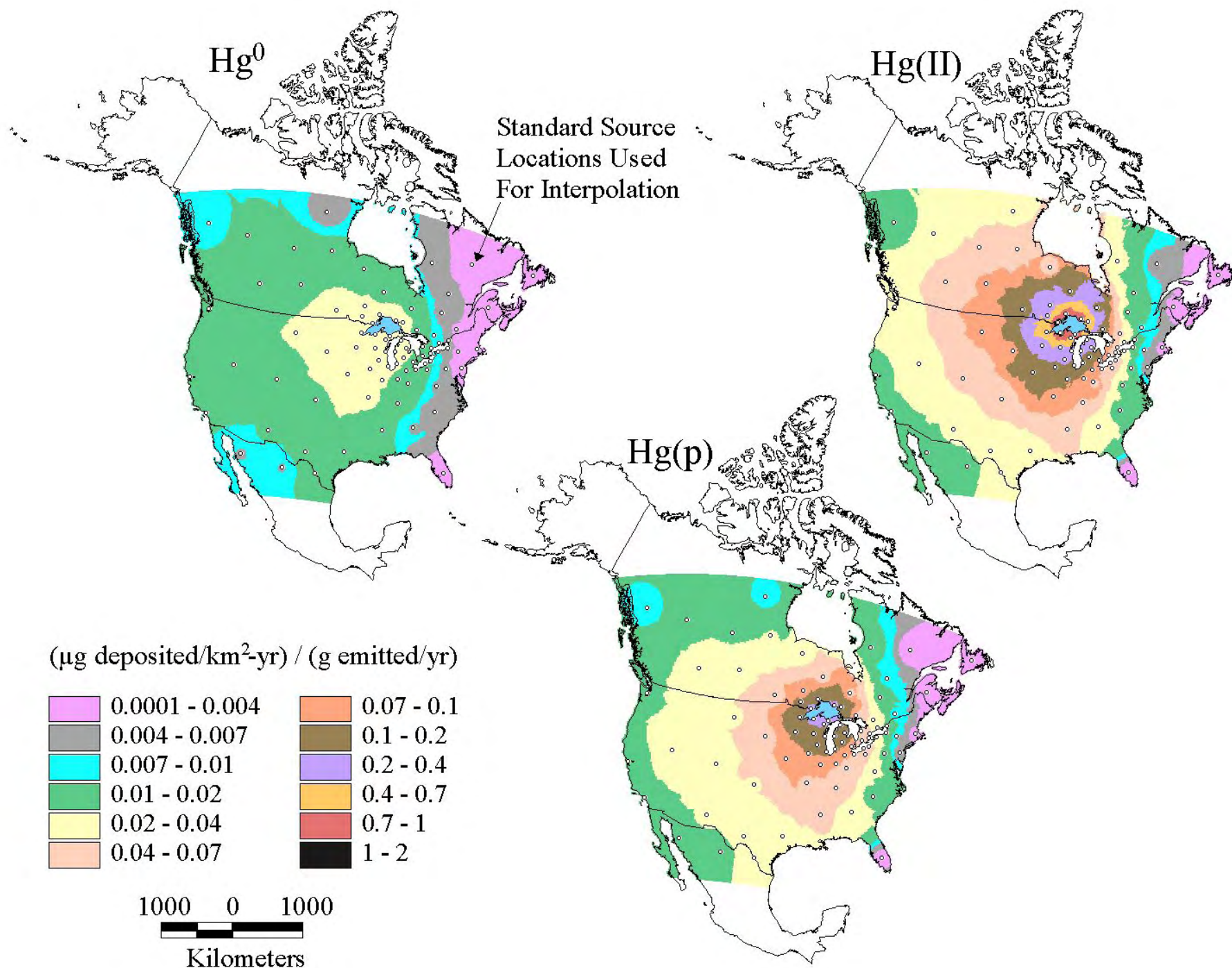
## Transfer Coefficients

- refer to *hypothetical* emissions;  
[are independent of actual emissions]
- can be formulated with different units  
[in this example: total Hg deposition flux  
( $\mu\text{g}/\text{km}^2\text{-yr}$ ) / emissions (g/yr)]
- will depend on the pollutant  
[in this example: Hg(0)]
- will depend on the receptor  
[in this example: Lake Superior]
- and the time period being modeled  
[in this example: entire year 1996]



( $\mu\text{g}$  deposited/ $\text{km}^2\text{-yr}$ ) / (g emitted/yr)







## Modeling the atmospheric transport and deposition of mercury to the Great Lakes<sup>☆</sup>

Mark Cohen,<sup>a,\*</sup> Richard Artz,<sup>a</sup> Roland Draxler,<sup>a</sup> Paul Miller,<sup>b</sup> Laurier Poissant,<sup>c</sup>  
David Niemi,<sup>d</sup> Dominique Ratté,<sup>d</sup> Marc Deslauriers,<sup>d</sup> Roch Duval,<sup>e</sup> Rachelle Laurin,<sup>e,1</sup>  
Jennifer Slotnick,<sup>f</sup> Todd Nettesheim,<sup>g</sup> and John McDonald<sup>h</sup>

<sup>a</sup>NOAA Air Resources Laboratory, 1315 East West Highway, BRL, Room 316, Silver Spring, MD 20910, USA

<sup>b</sup>Commission for Environmental Cooperation, Montreal, Que., Canada

<sup>c</sup>Atmospheric Toxic Processes Section, Meteorological Service of Canada, Environment Canada–Quebec region, Montreal, Que., Canada

<sup>d</sup>Pollutant Data Branch, Environment Canada, Hull, Que., Canada

<sup>e</sup>Bioremediation Monitoring and Reporting Branch, Ontario Ministry of the Environment, Toronto, Ont., Canada

<sup>f</sup>University of California, Berkeley, CA, USA

<sup>g</sup>US EPA Great Lakes National Program Office, Chicago, IL, USA

<sup>h</sup>International Joint Commission, Windsor, Ont., Canada

Received 28 August 2003; received in revised form 12 November 2003; accepted 19 November 2003

### Abstract

A special version of the NOAA HYSPLIT-4 model has been developed and used to estimate the atmospheric fate and transport of mercury in a North American modeling domain. Spatial and chemical interpolation procedures were used to expand the modeling results and provide estimates of the contribution of each source in a 1996 anthropogenic US/Canadian emissions inventory to atmospheric mercury deposition to the Great Lakes. While there are uncertainties in the emissions inventories and ambient data suitable for model evaluation are scarce, model results were found to be reasonably consistent with wet deposition measurements in the Great Lakes region and with independent measurement-based estimates of deposition to Lake Michigan. Sources up to 2000 km from the Great Lakes contributed significant amounts of mercury through atmospheric transport and deposition. While there were significant contributions from incineration and metallurgical sources, coal combustion was generally found to be the largest contributor to atmospheric mercury deposition to the Great Lakes.

Published by Elsevier Inc.

**Keywords:** Mercury; Atmospheric deposition; Great Lakes; Source-receptor modeling; Emissions

Mercury contamination in the Great Lakes and many other ecosystems is increasingly being recognized as a serious environmental concern. The dominant route of human exposure to mercury is through fish consumption, and significant portions of the general population are believed to be consuming toxicologically significant levels of mercury (e.g., National Research Council, 2000). Historical discharges—e.g., from chlor-alkali production using the mercury-cell process—are believed to have caused large accumulations of mercury in

sediments in Lake Erie and Lake Ontario (Marvin et al., 2003). As these discharges have been substantially reduced, atmospheric deposition is now believed to be a more significant loading pathway for these lakes. Mass balance calculations for Lake Michigan (Mason and Sullivan, 1997) and Lake Superior (Dolan et al., 1993) indicate that atmospheric deposition accounts for approximately 75% of the overall mercury loading to these lakes.

While there have been several mercury modeling efforts in North America (Bullock et al., 1998; Bullock and Bachme, 2002; Dvosch et al., 1998; Lin et al., 2001; Pai et al., 1997; Seigneur et al., 2000, 2001, 2003a, b; Shannon and Voldner, 1995; Xu et al., 2000a–c), none has developed detailed source–receptor relationships for the Great Lakes, as advocated in Annex 15 of the Great

<sup>☆</sup>Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.environres.2003.11.007](http://doi:10.1016/j.environres.2003.11.007).

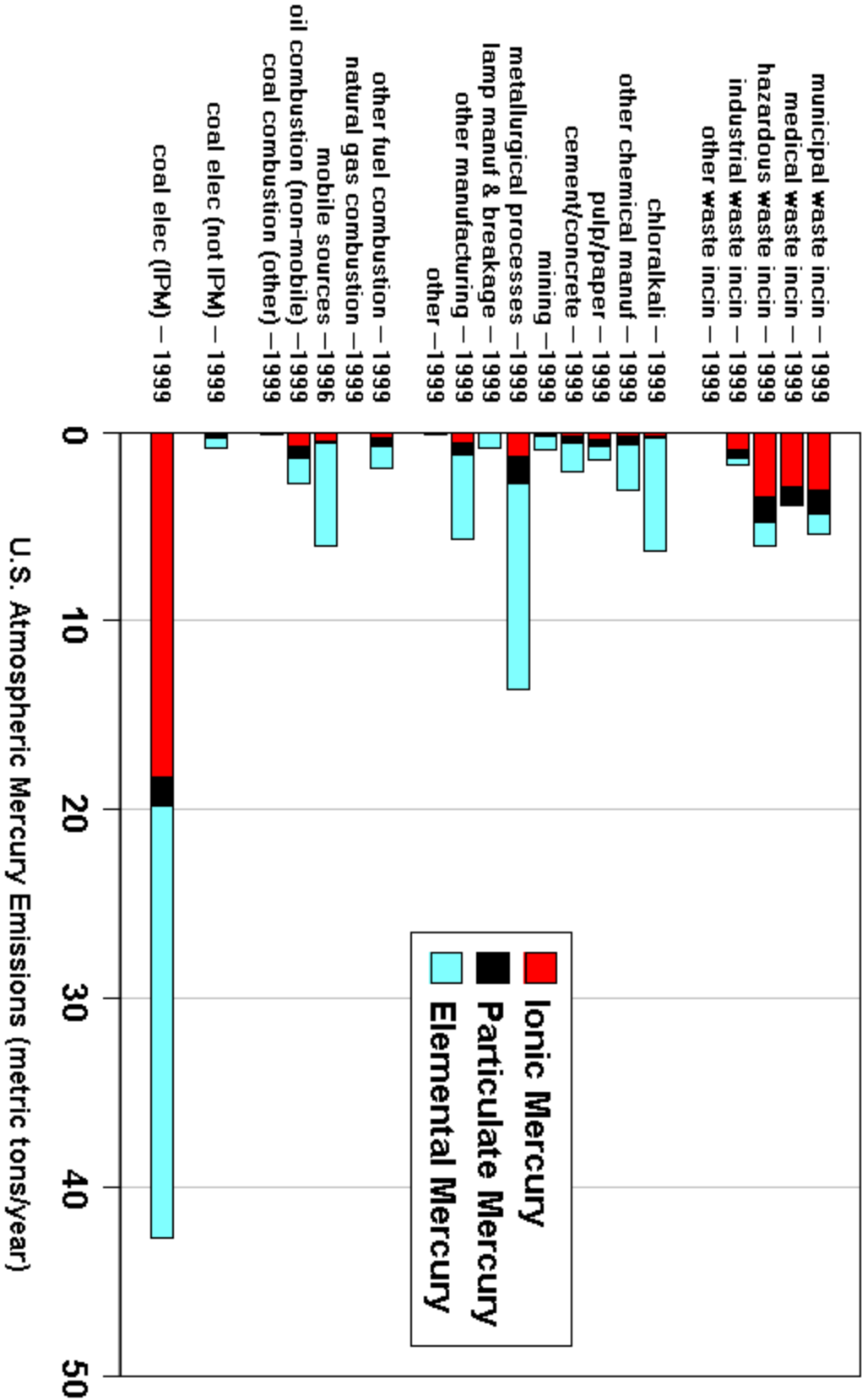
\*Corresponding author. Fax: +1 301-713-0119.

E-mail address: [mark.cohen@noaa.gov](mailto:mark.cohen@noaa.gov) (M. Cohen).

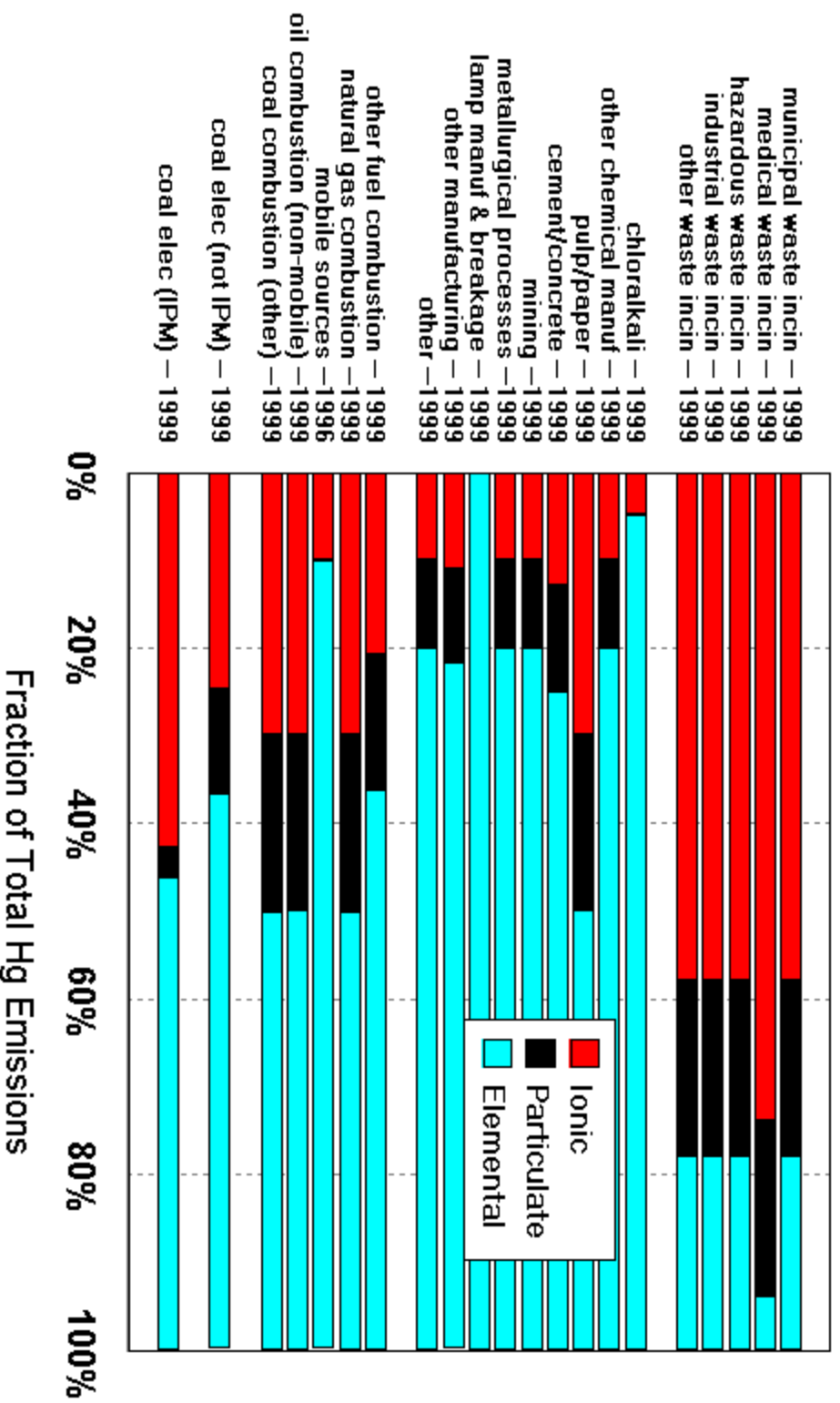
Current address: ICPRA Canada/The Institute of Environmental Research, Concord, Ontario, Canada.

# **Mercury Emissions Inventory**

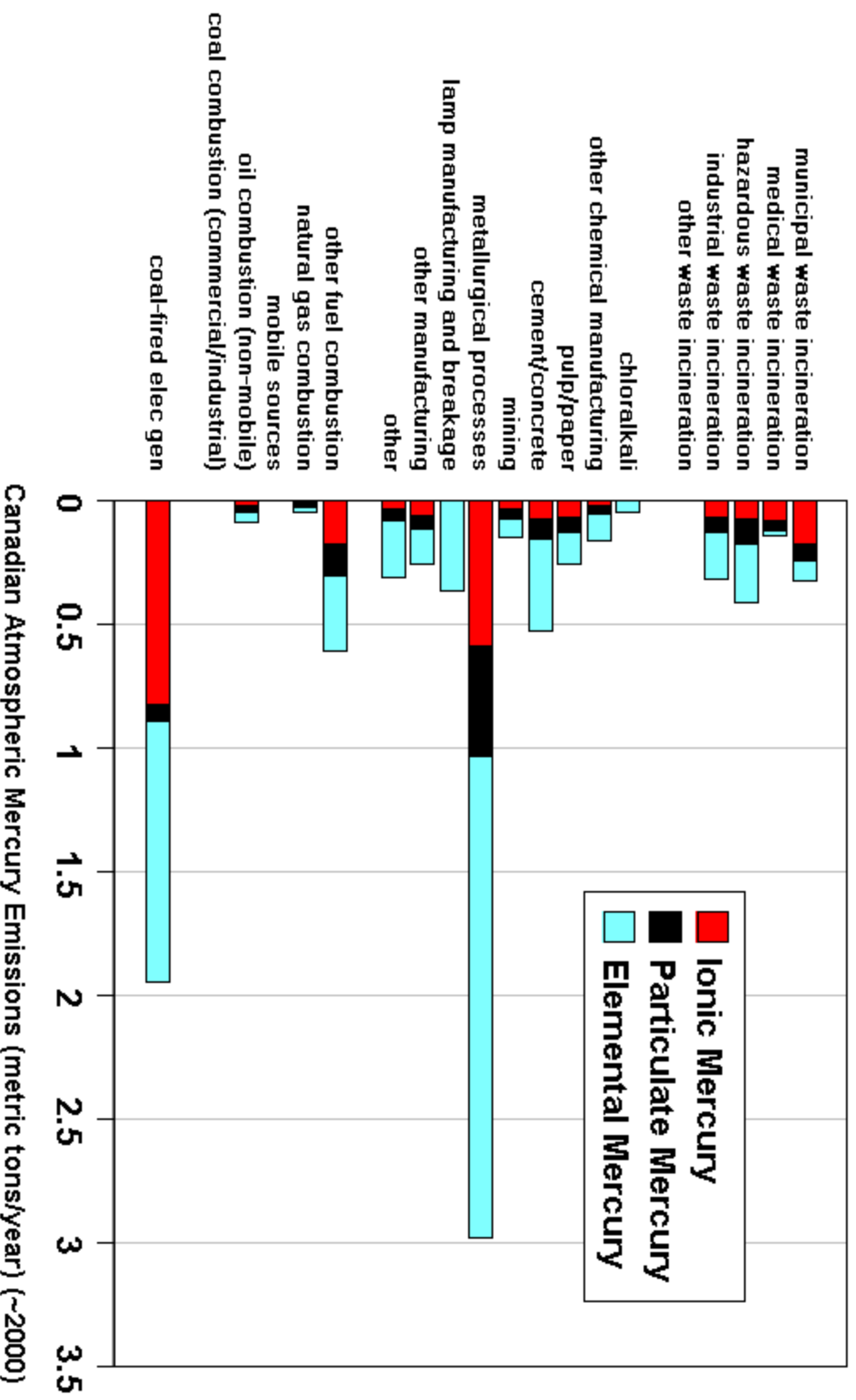
# Estimated 1999 U.S. Atmospheric Anthropogenic Mercury Emissions



# Estimated Speciation Profile for 1999 U.S. Atmospheric Anthropogenic Mercury Emissions

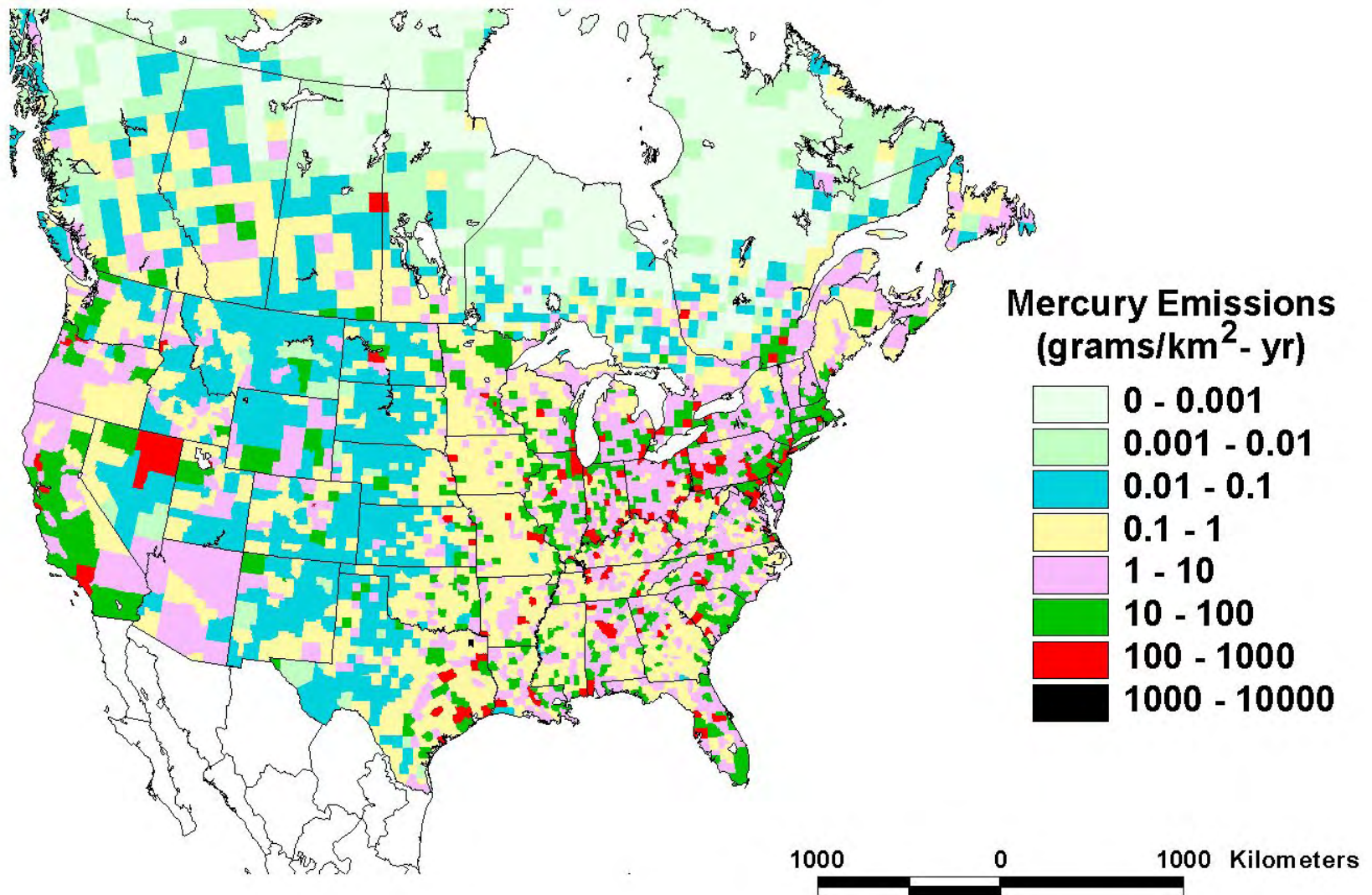


# Estimated 2000 Canadian Atmospheric Anthropogenic Mercury Emissions

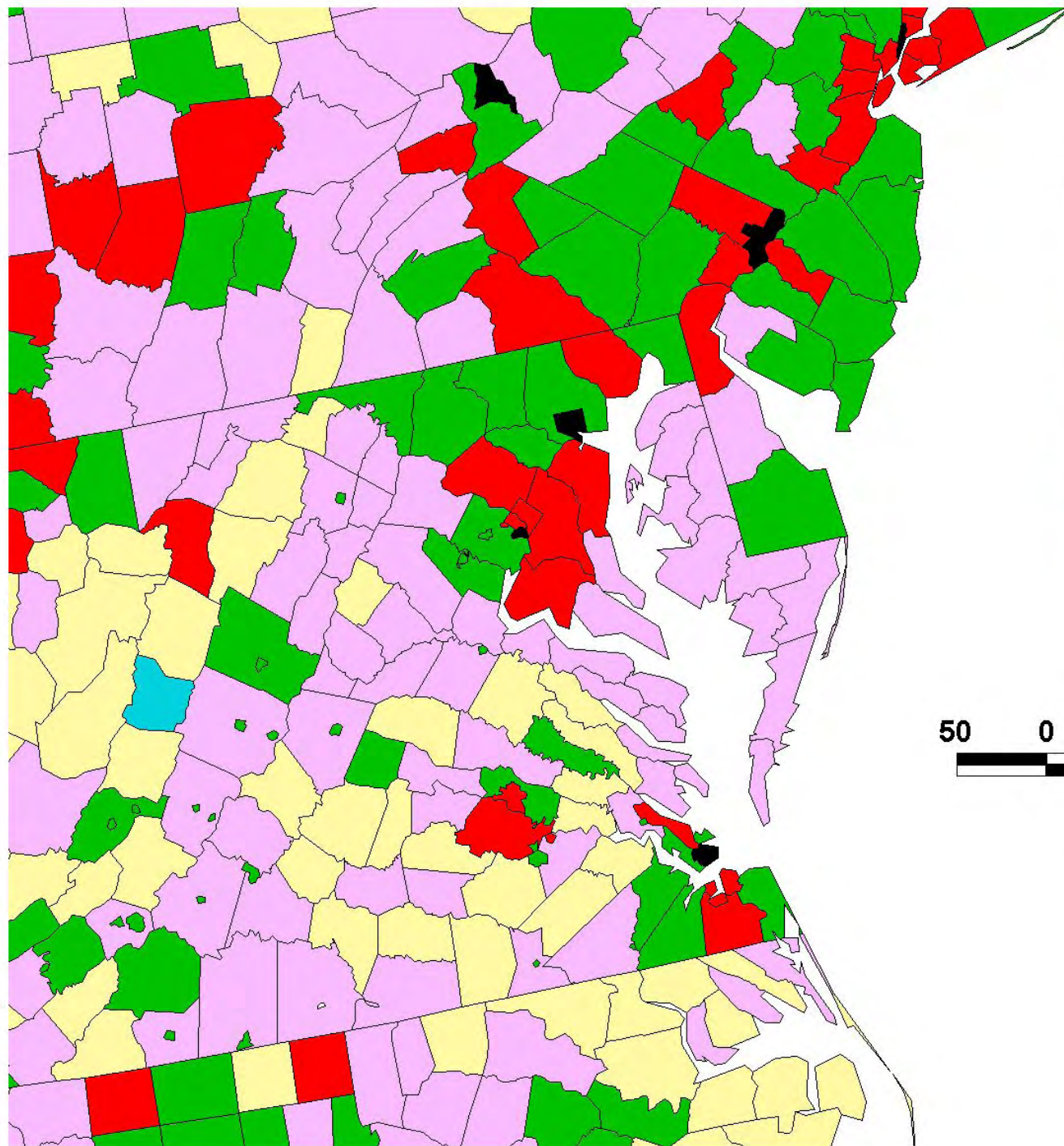




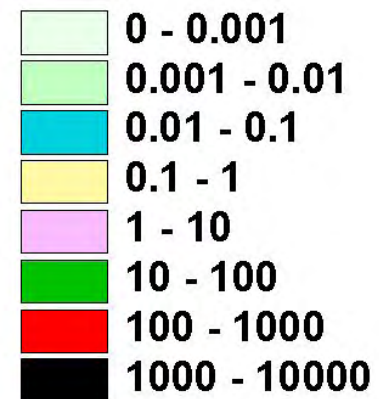
## Geographic Distribution of Estimated Anthropogenic Mercury Emissions in the U.S. (1999) and Canada (2000)





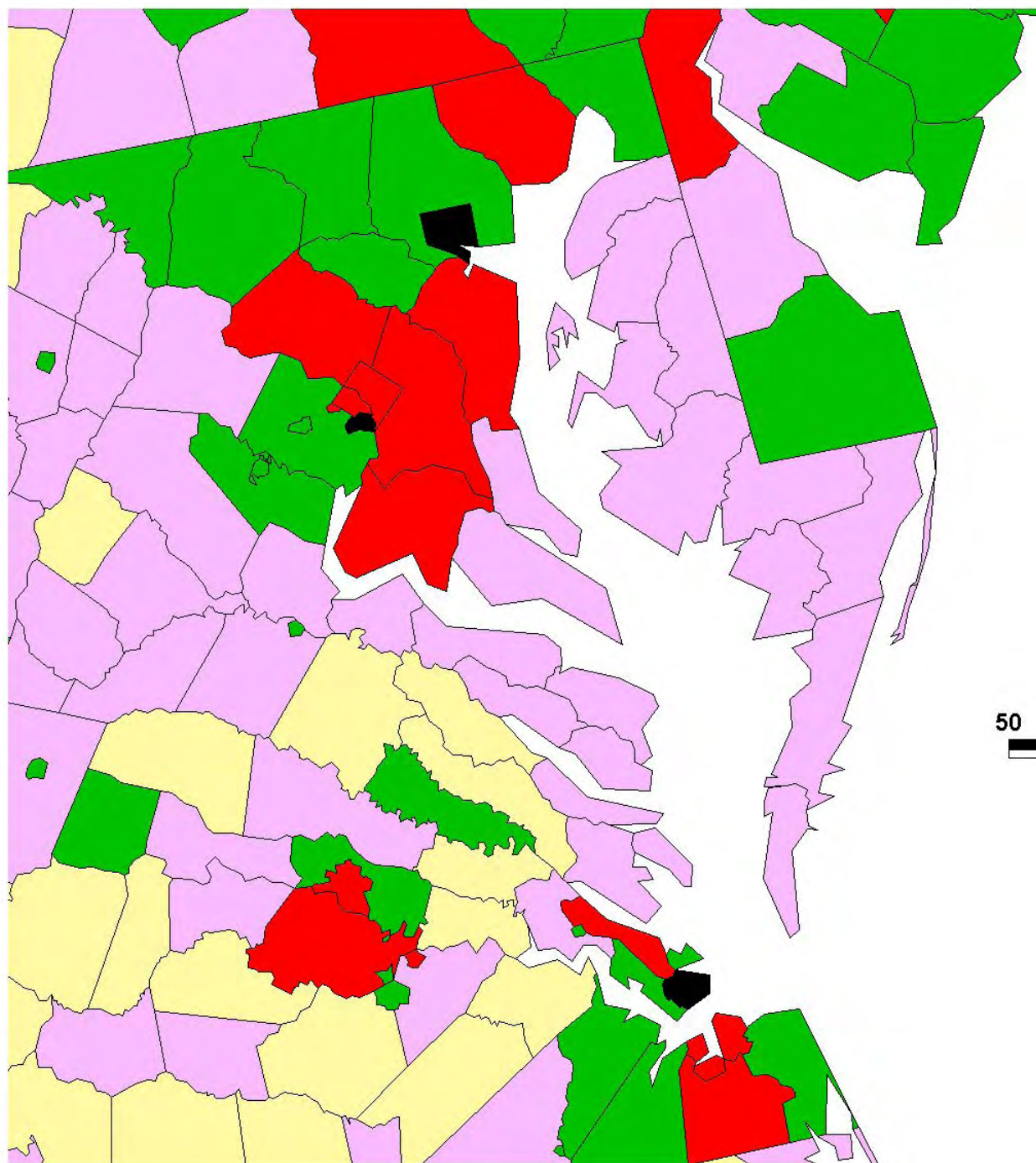


**Mercury Emissions  
(grams/km<sup>2</sup>- yr)**

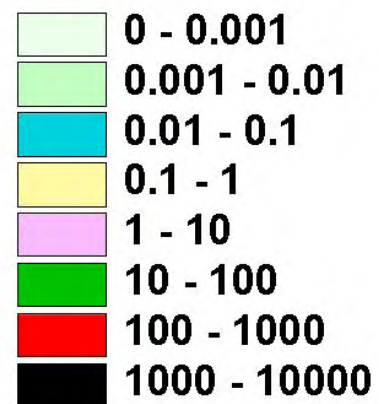


50 0 50 100 Kilometers





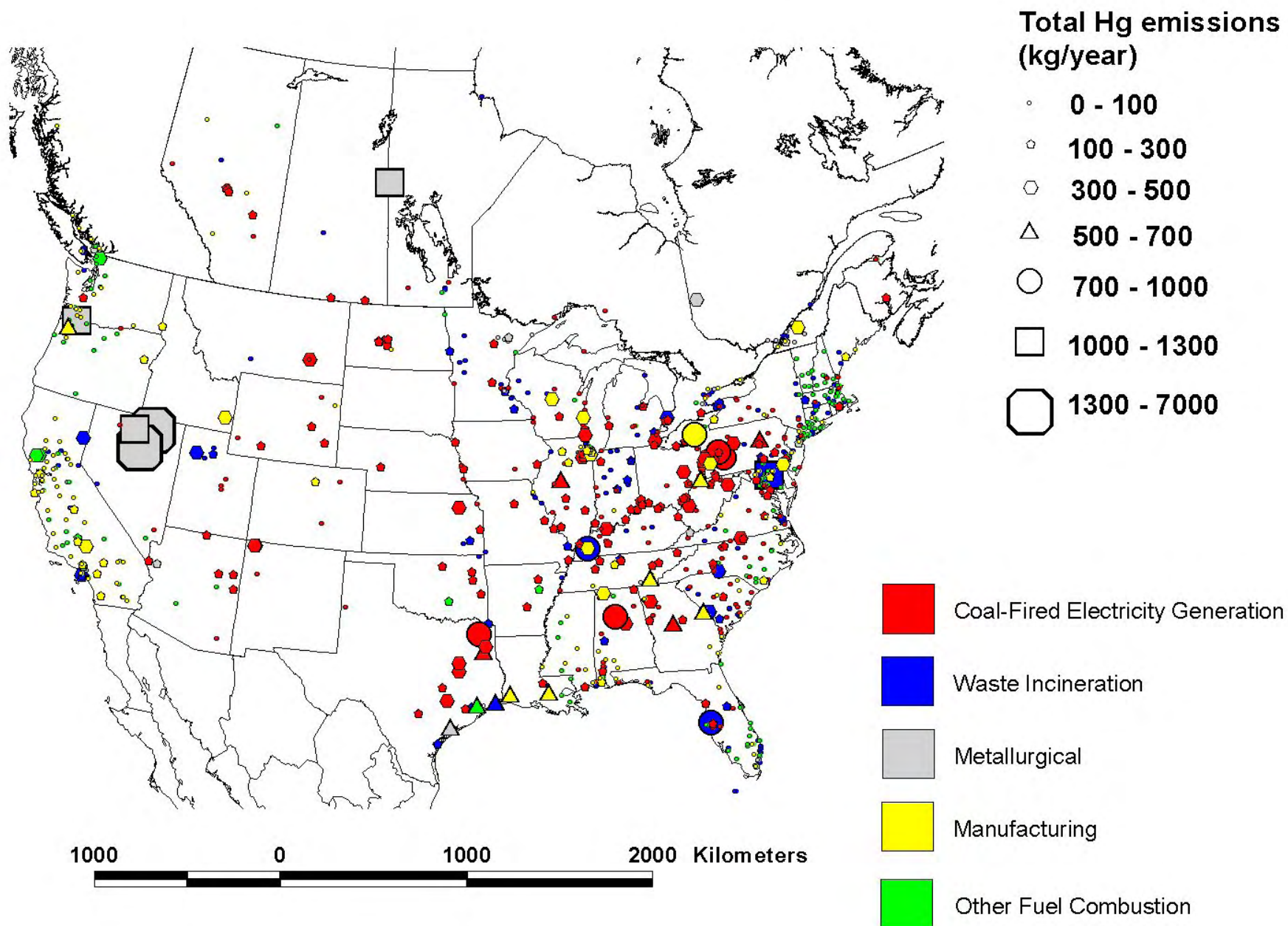
**Mercury Emissions  
(grams/km<sup>2</sup>- yr)**

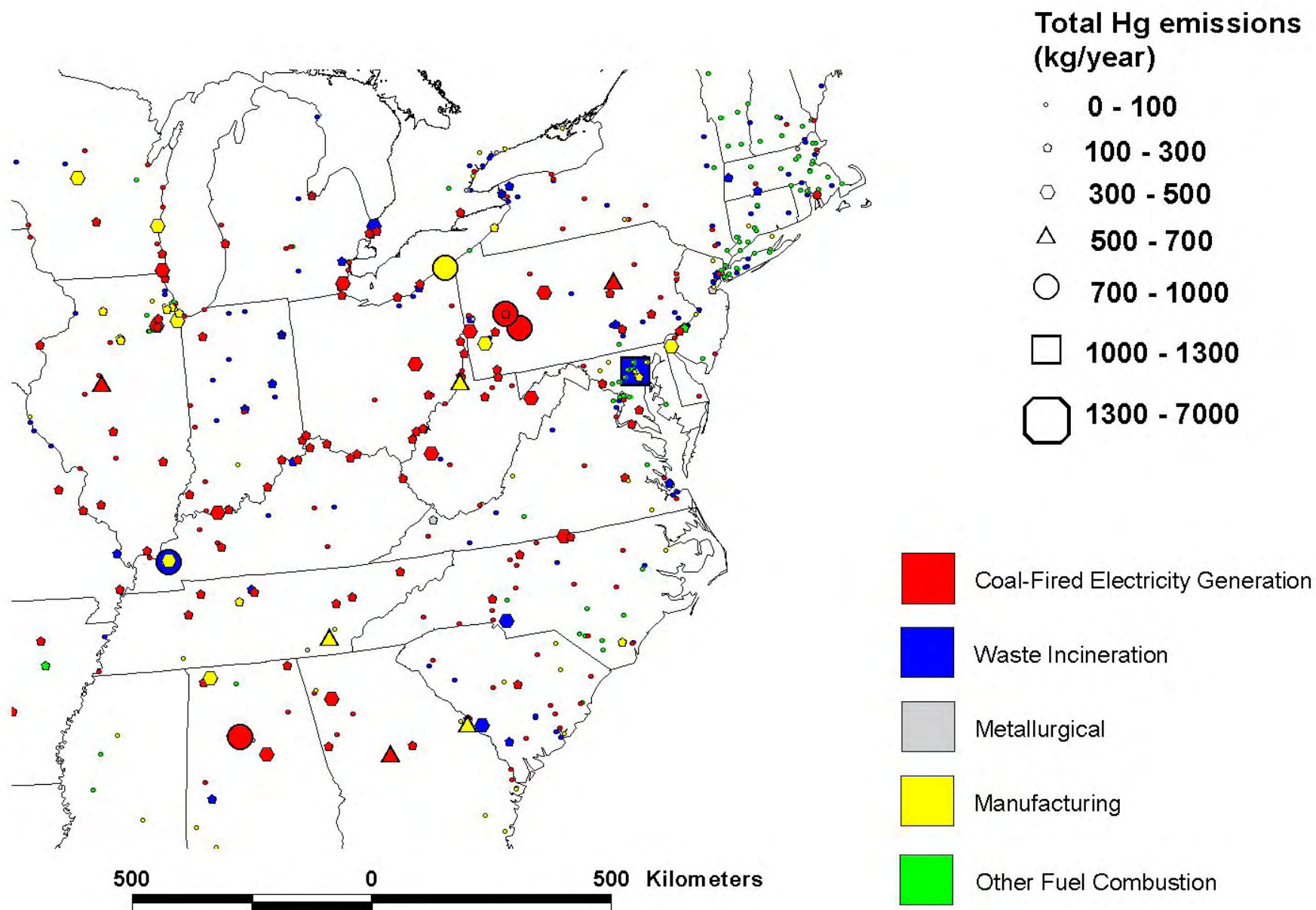


50 0 50 Kilometers



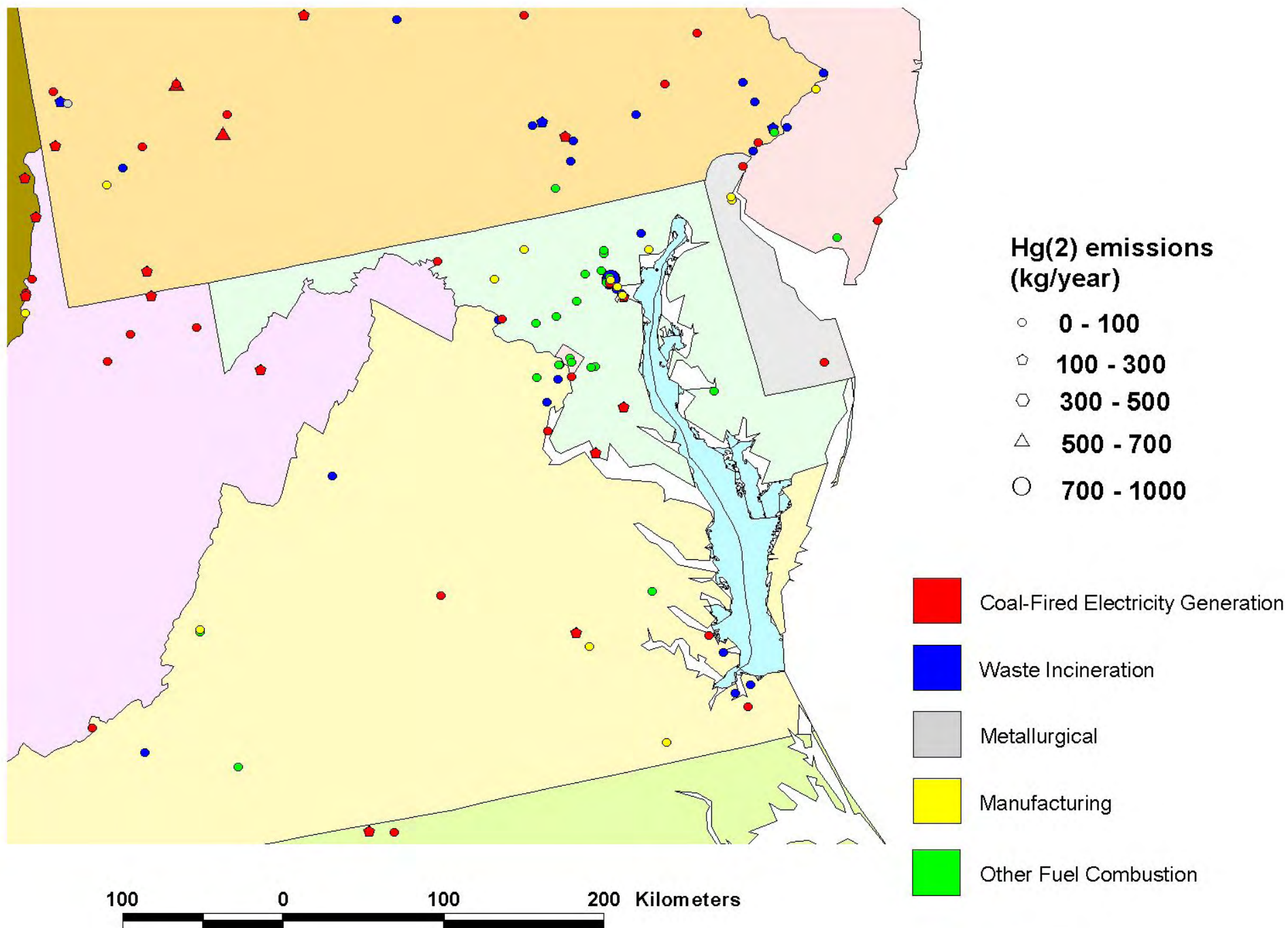




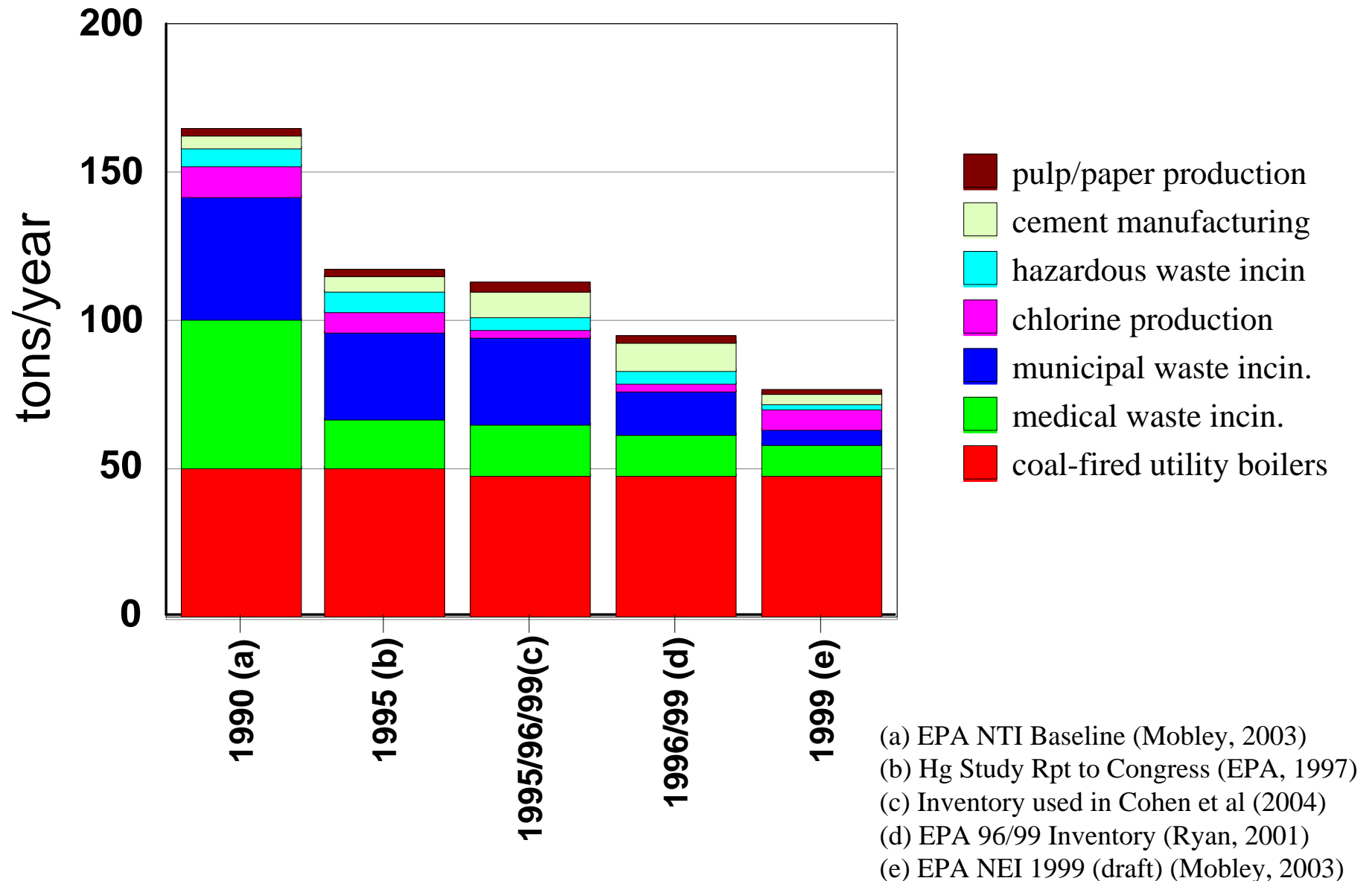


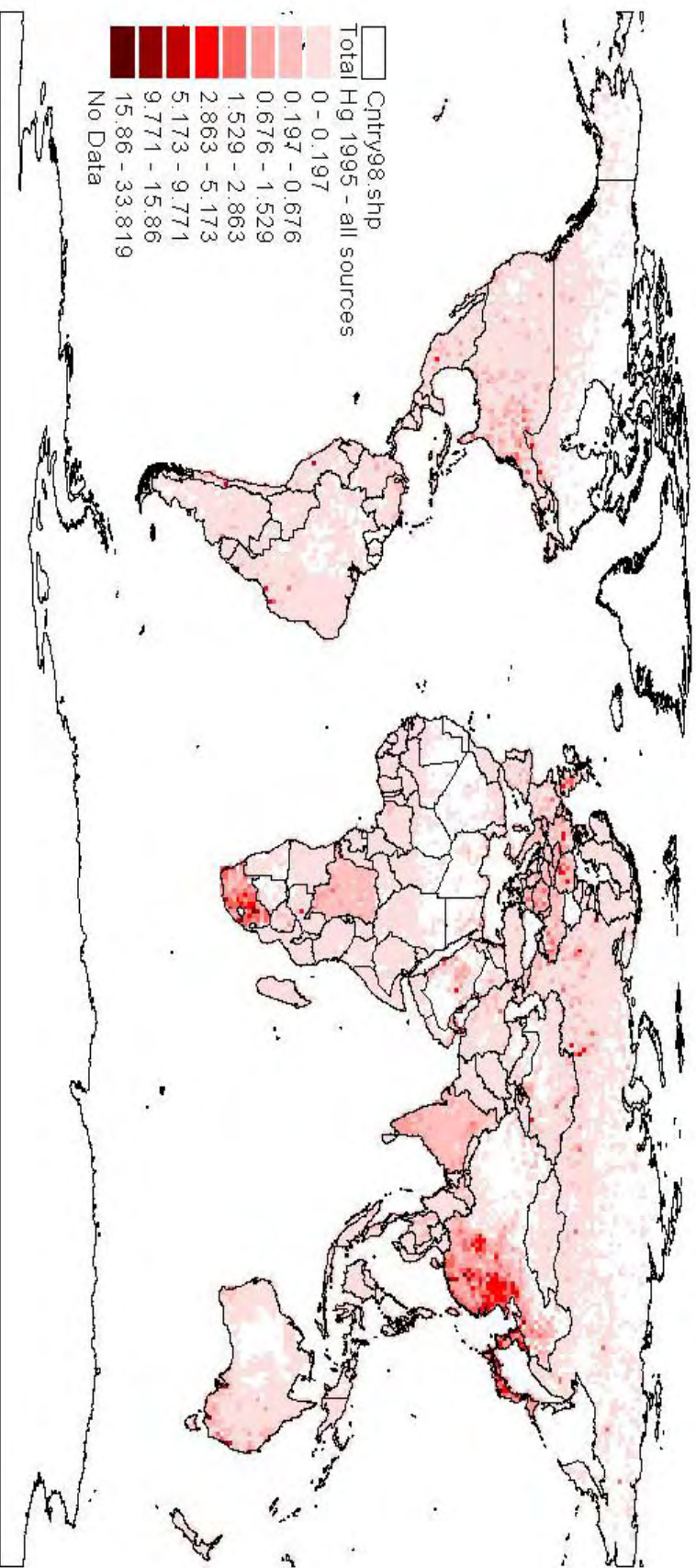






## Reported trends in U.S. atmospheric mercury emissions 1990-1999 (selected source categories)



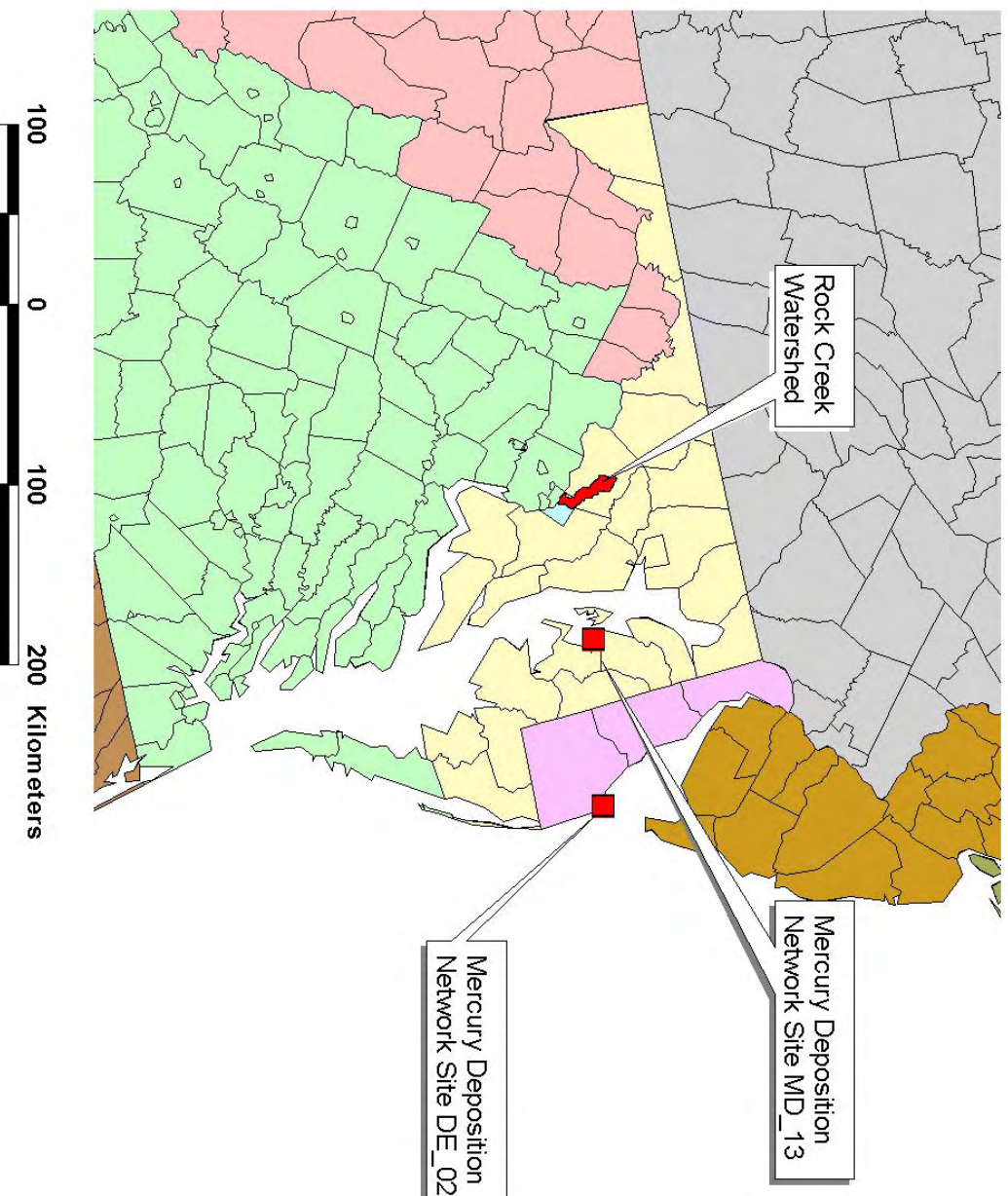


1995 Global Hg Emissions Inventory  
Josef Pacyna, NILU, Norway (2001)

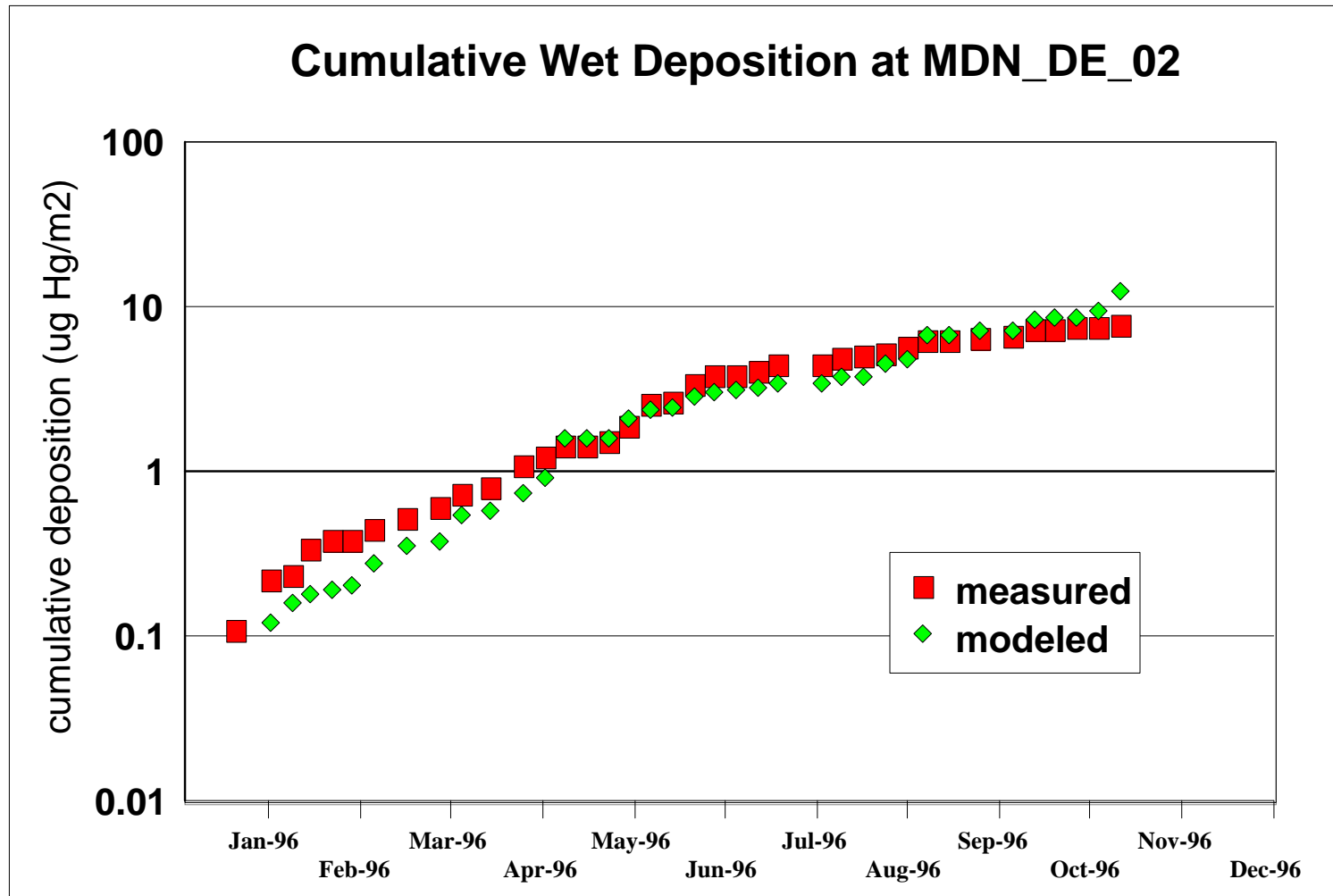


# **Model Evaluation**

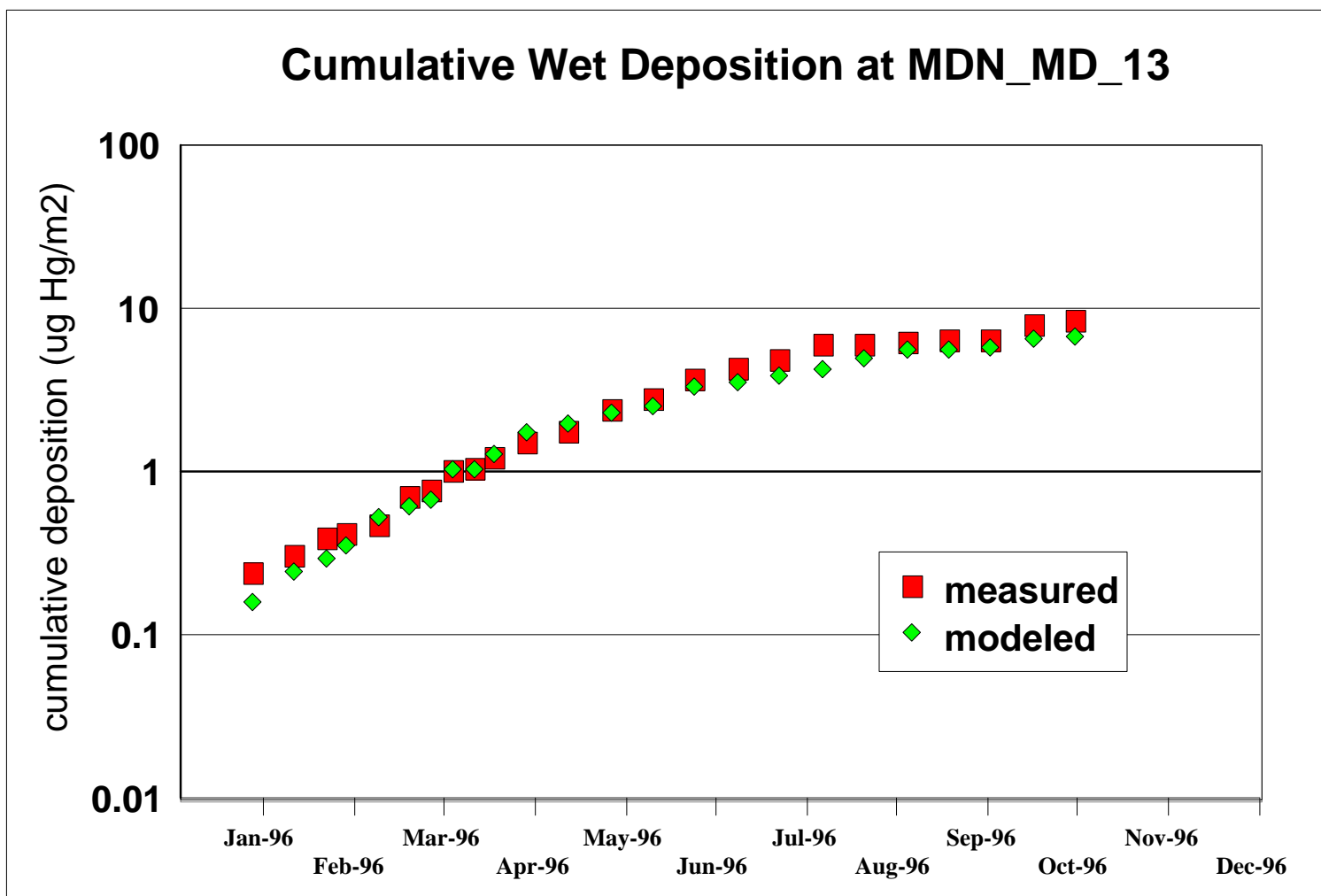
# Mercury Deposition Network Sites with 1996 data in the Chesapeake Bay Region



## Modeled vs. Measured Wet Deposition at Mercury Deposition Network Site DE\_02 during 1996

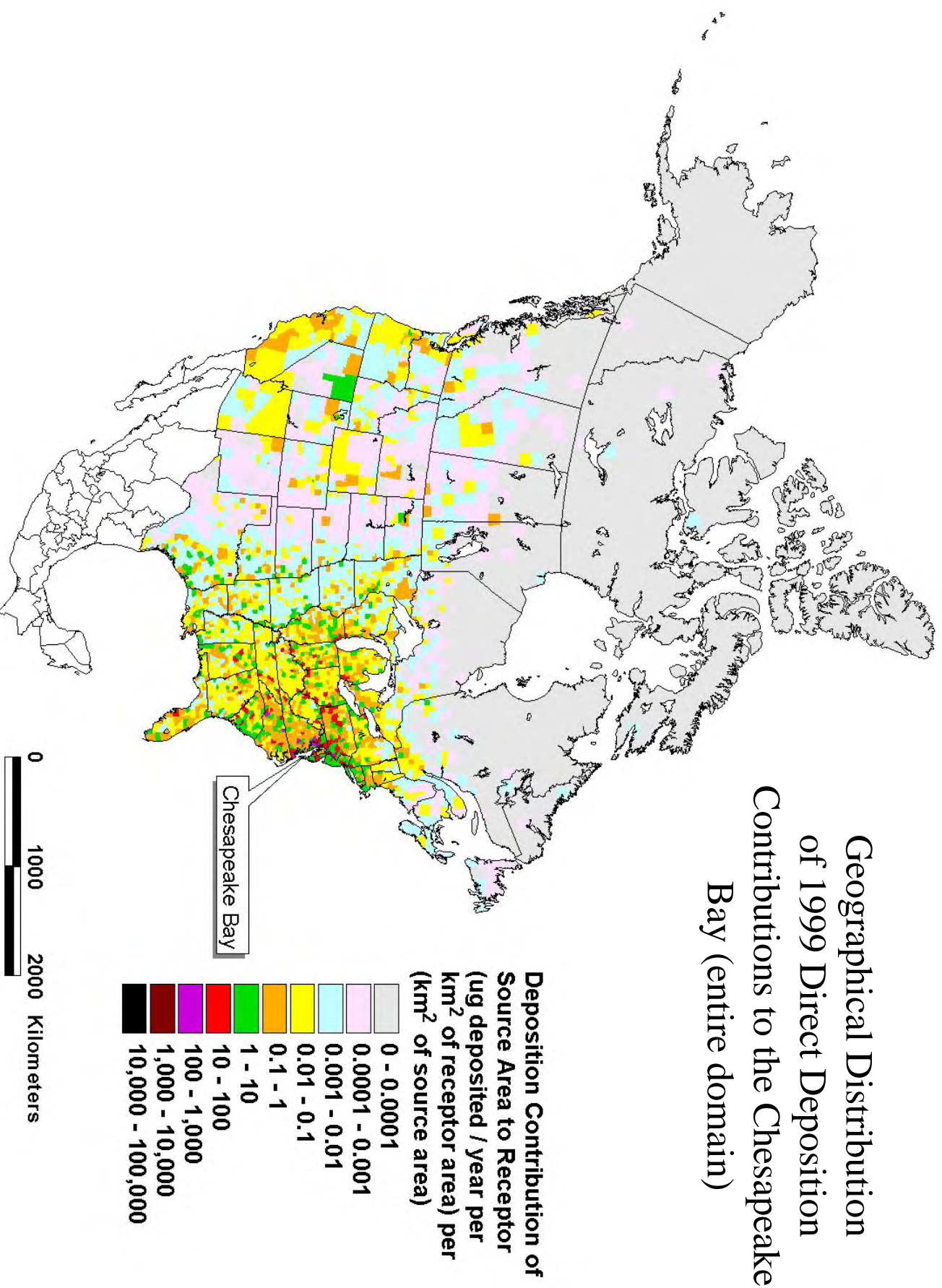


## Modeled vs. Measured Wet Deposition at Mercury Deposition Network Site MD\_13 during 1996



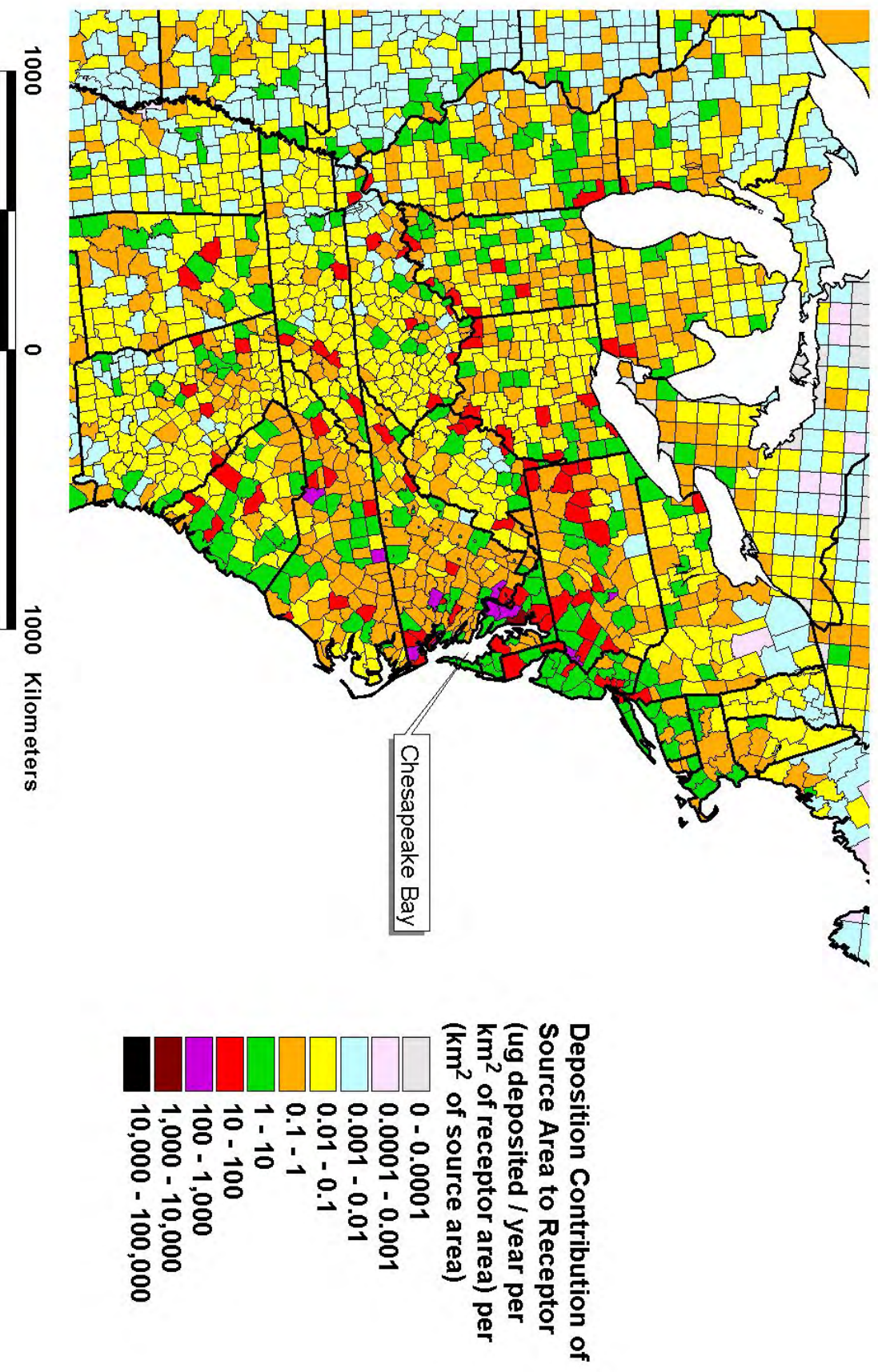
# **1999 Results for Chesapeake Bay**

# Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (entire domain)



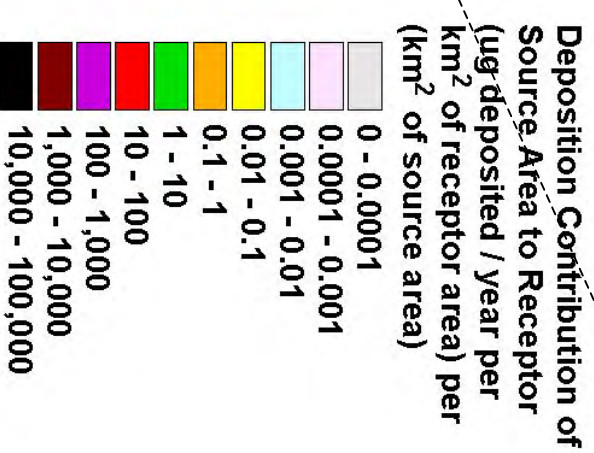
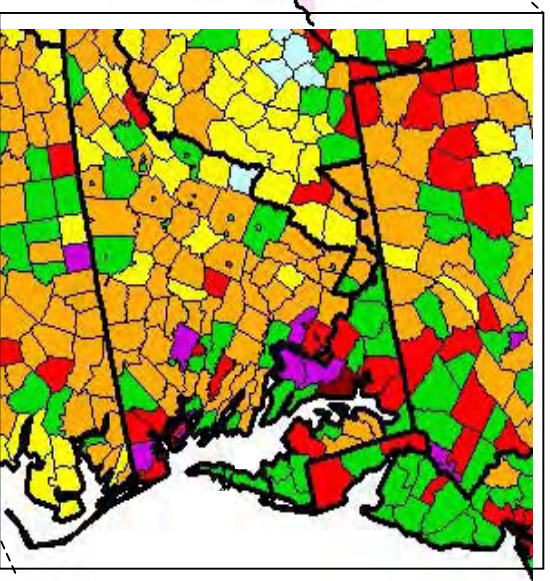
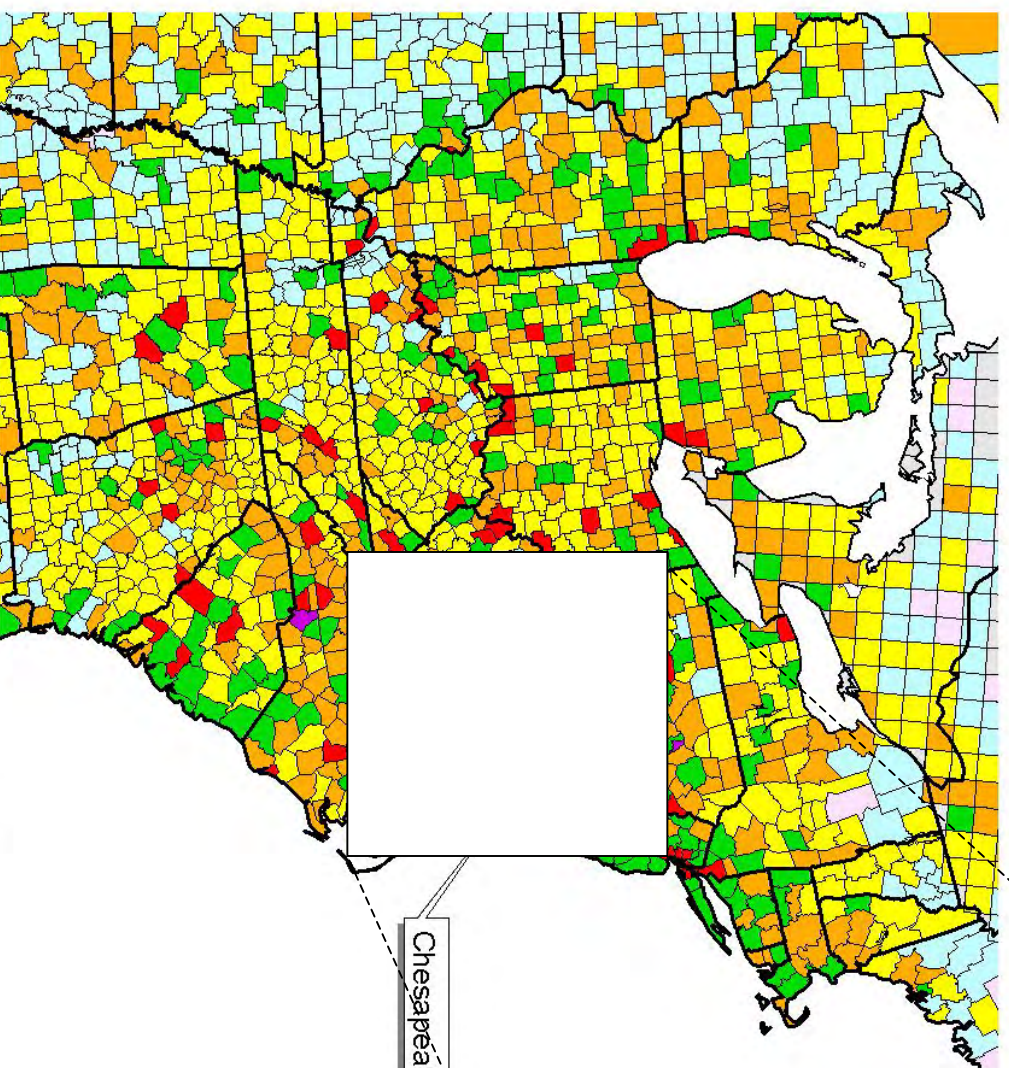


# Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (regional close-up)



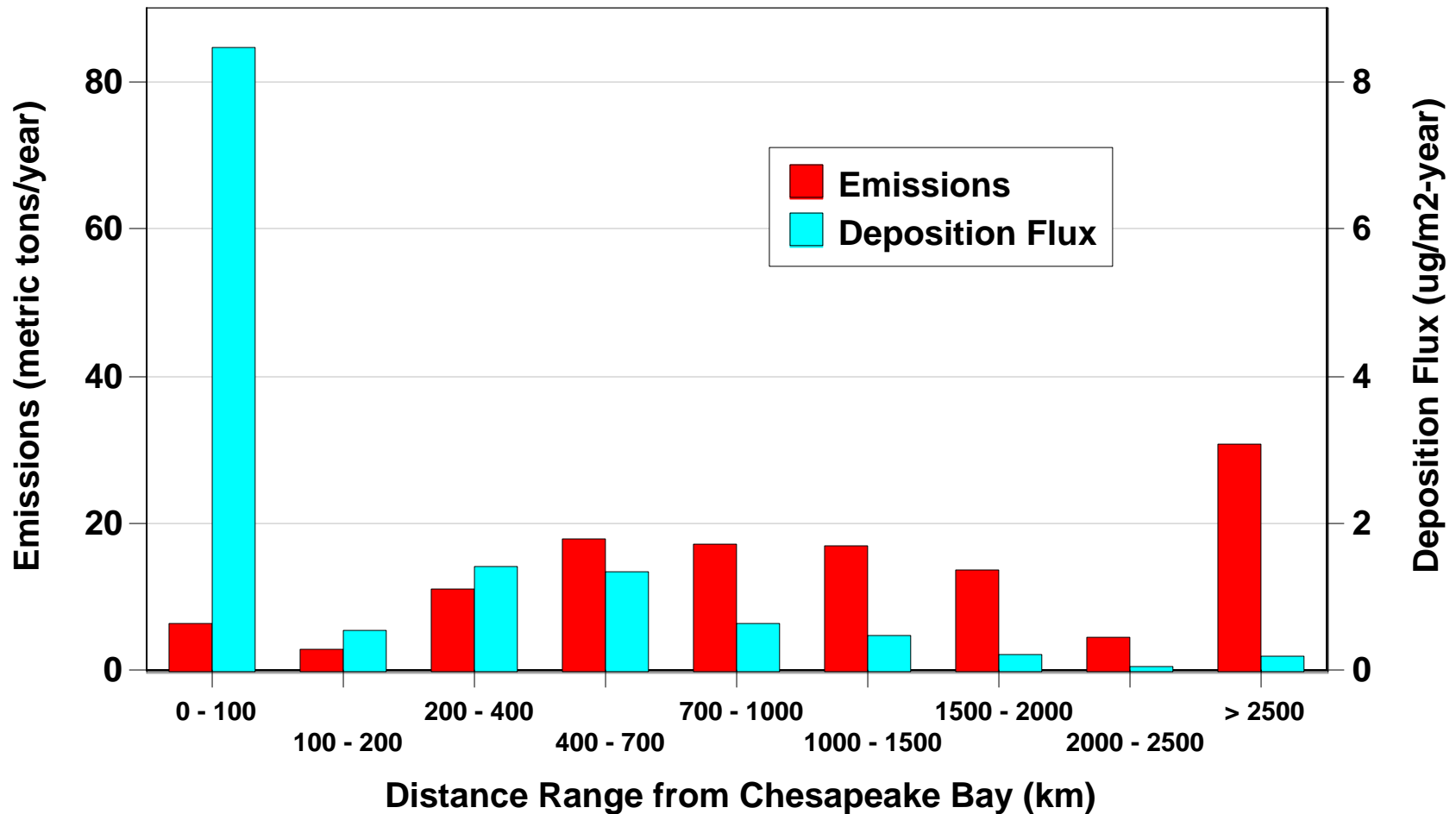


# Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (local close-up)

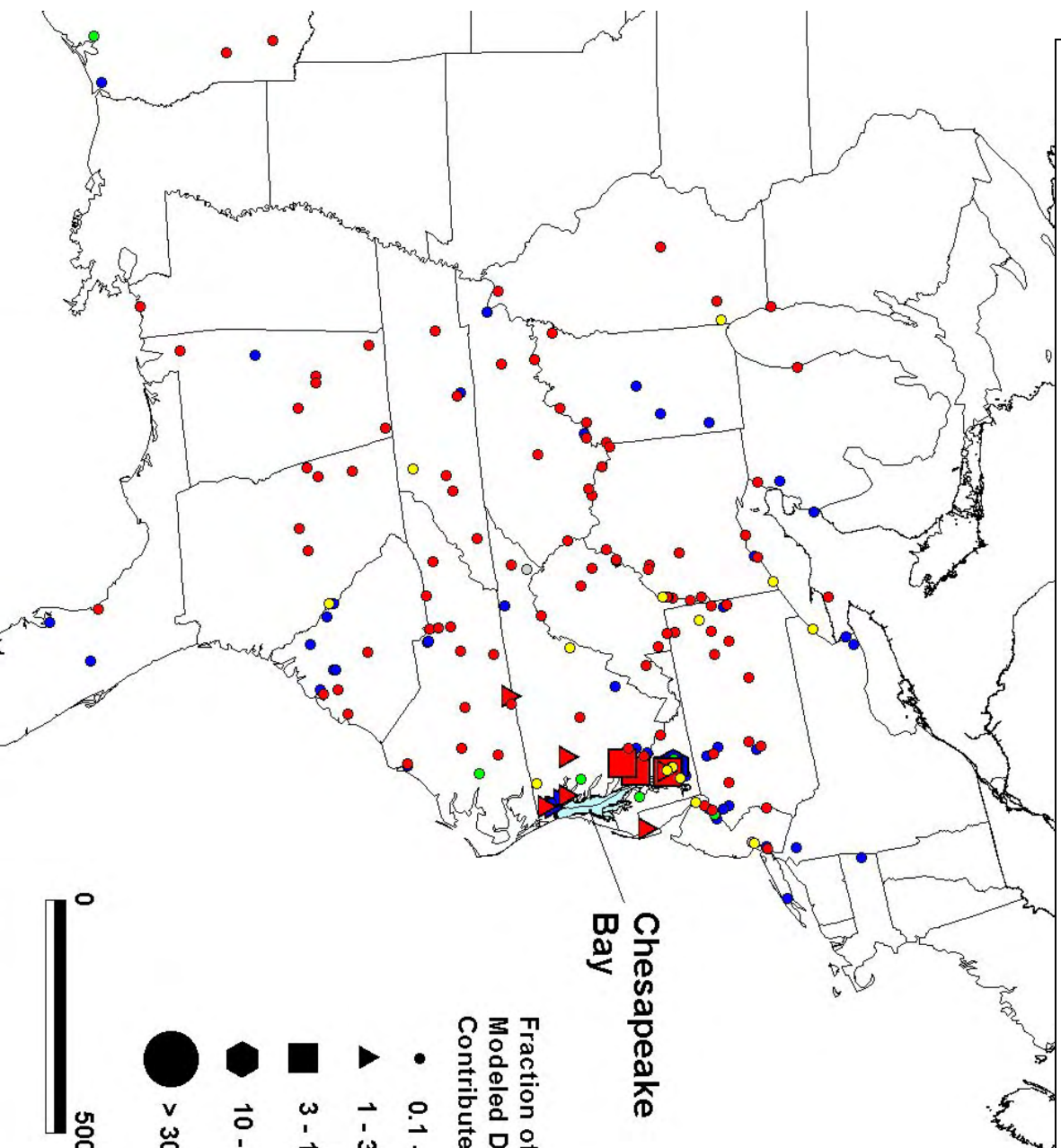




# Emissions and Direct Deposition Contributions from Different Distance Ranges Away From the Chesapeake Bay



# **Largest Regional Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay**



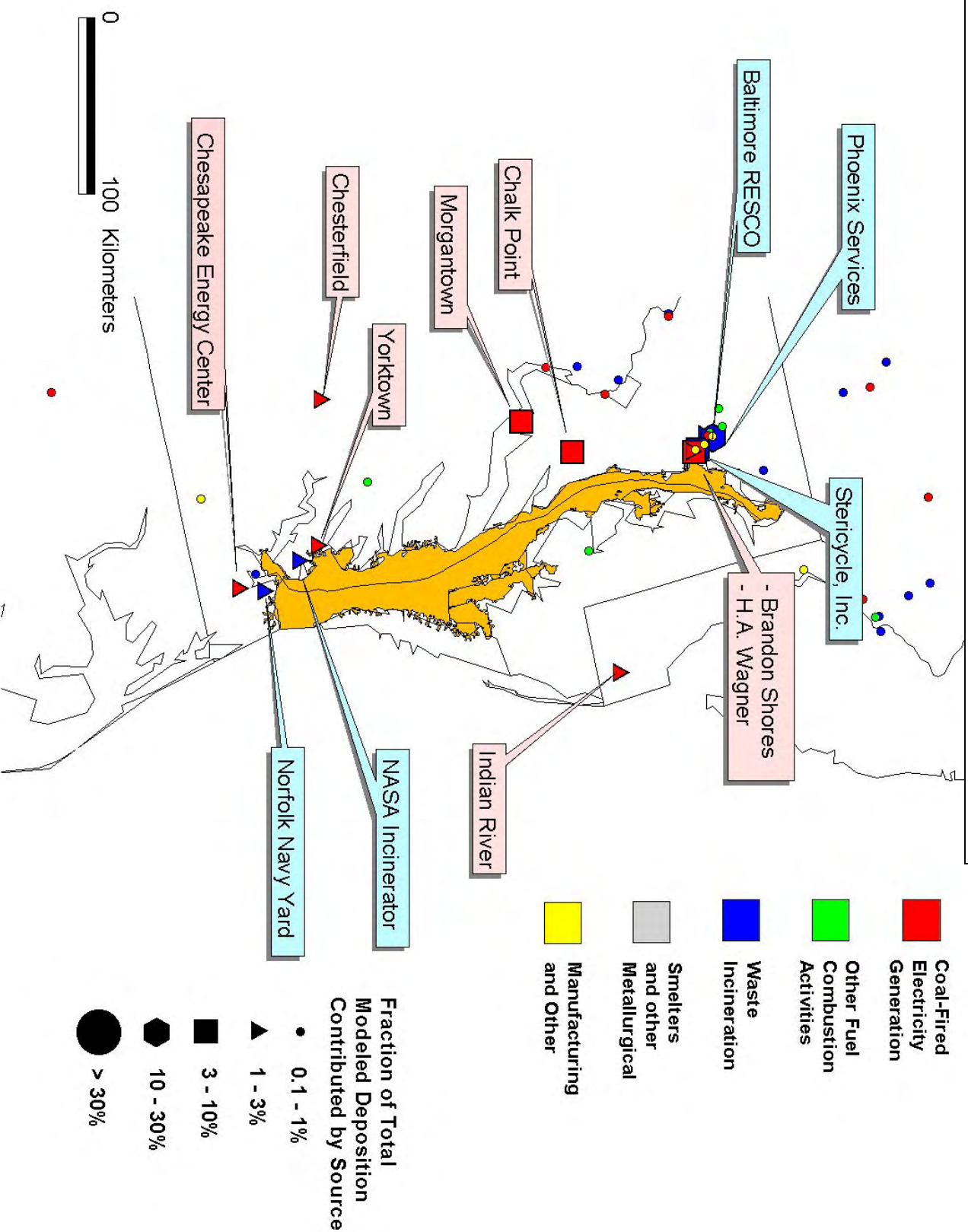
**Fraction of Total  
Modeled Deposition  
Contributed by Source**

- 0.1 - 1%
- ▲ 1 - 3%
- 3 - 10%
- ◼ 10 - 30%
- > 30%

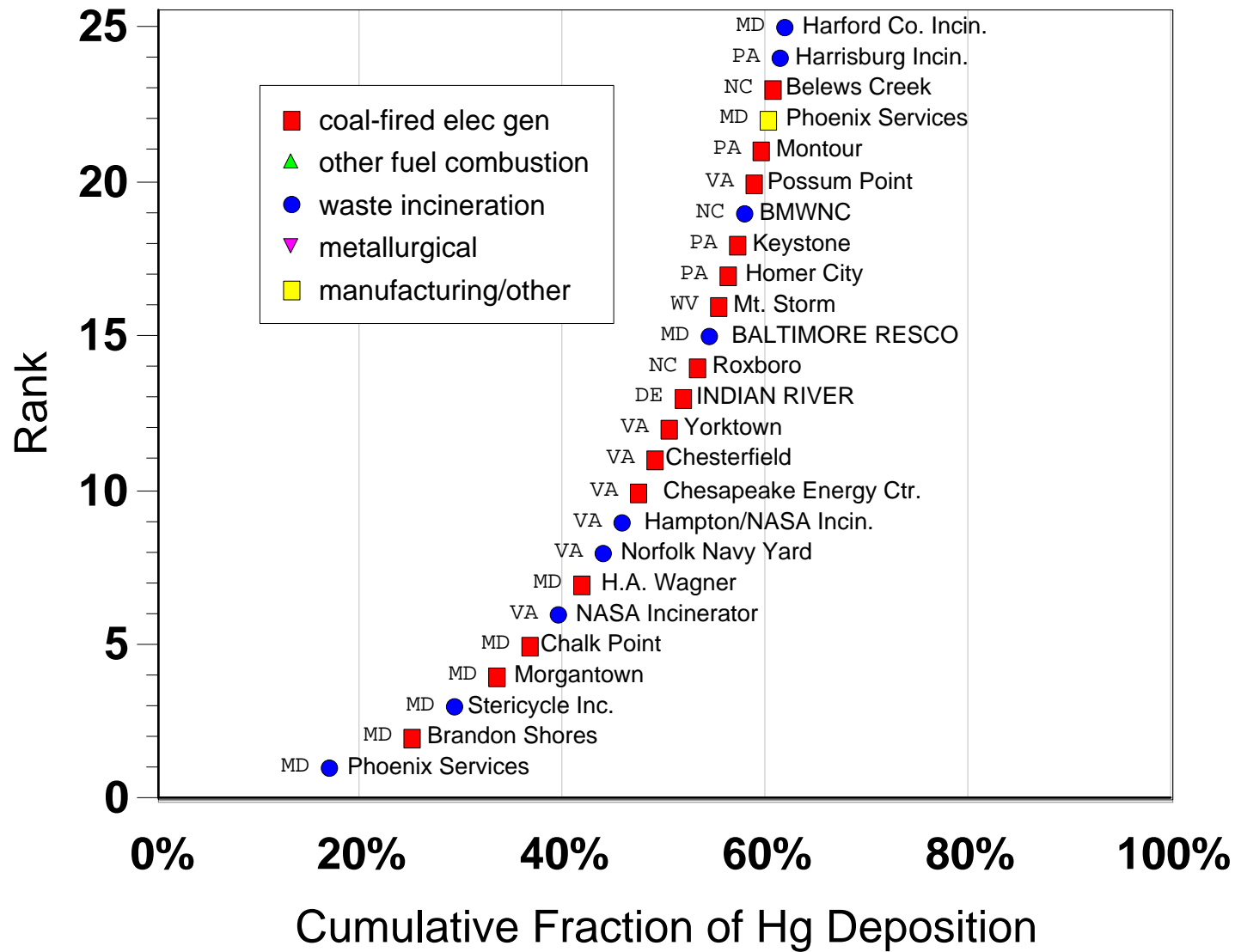
- Coal-Fired Electricity Generation
- Other Fuel Combustion Activities
- Waste Incineration
- Smelters and other Metallurgical
- Manufacturing and Other

0 500 Kilometers

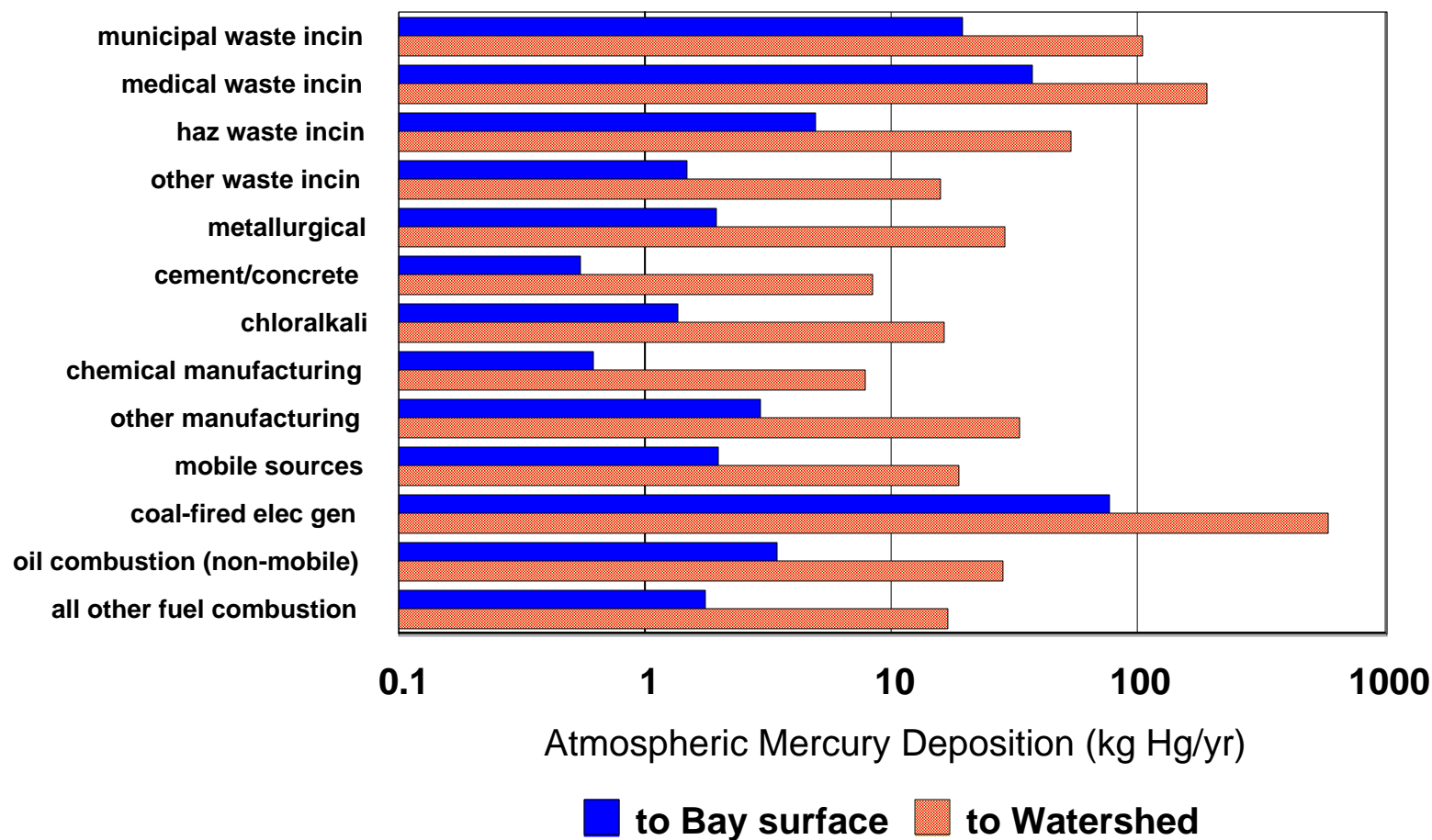
# Largest Local Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay



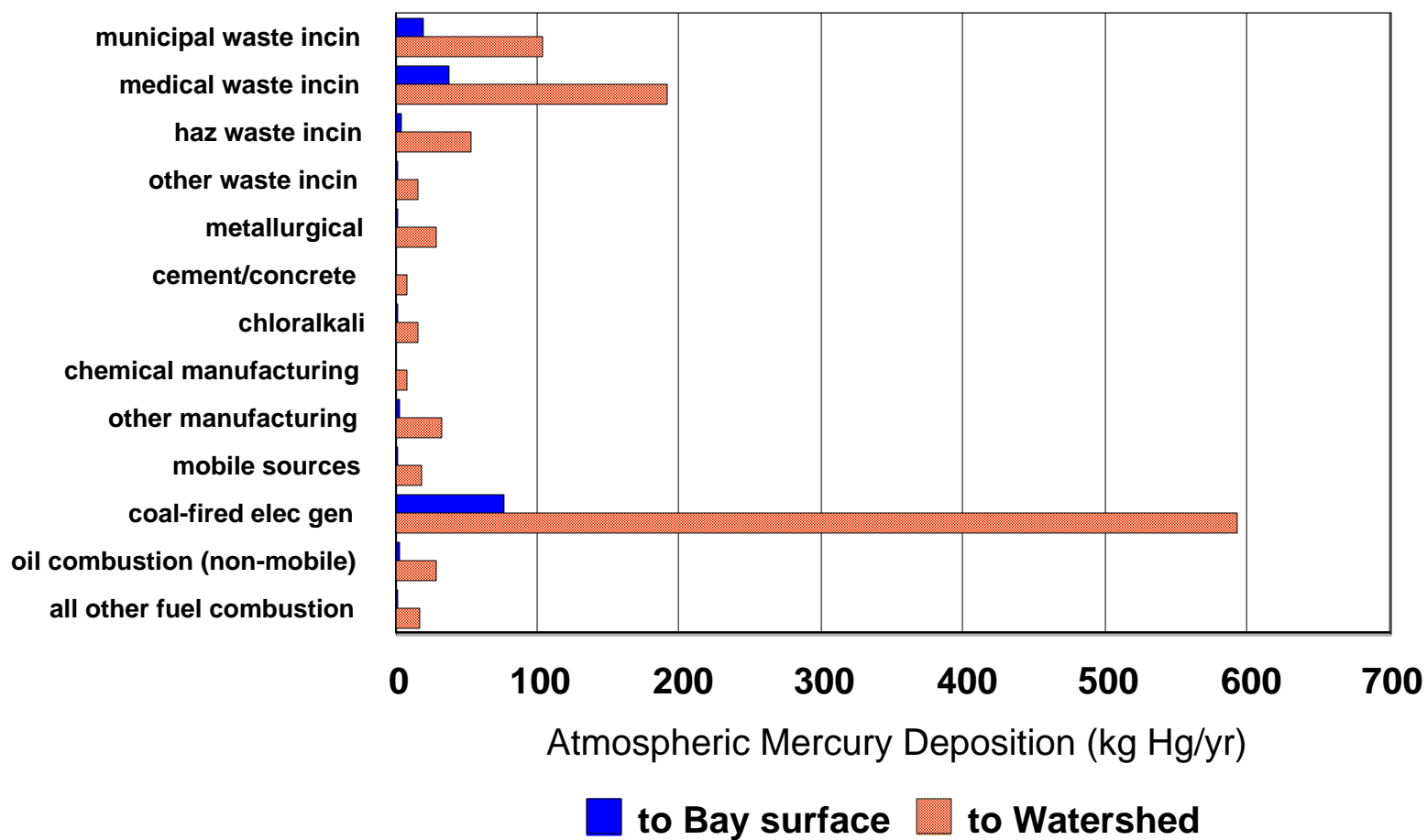
## Top 25 Contributors to 1999 Hg Deposition Directly to the Chesapeake Bay



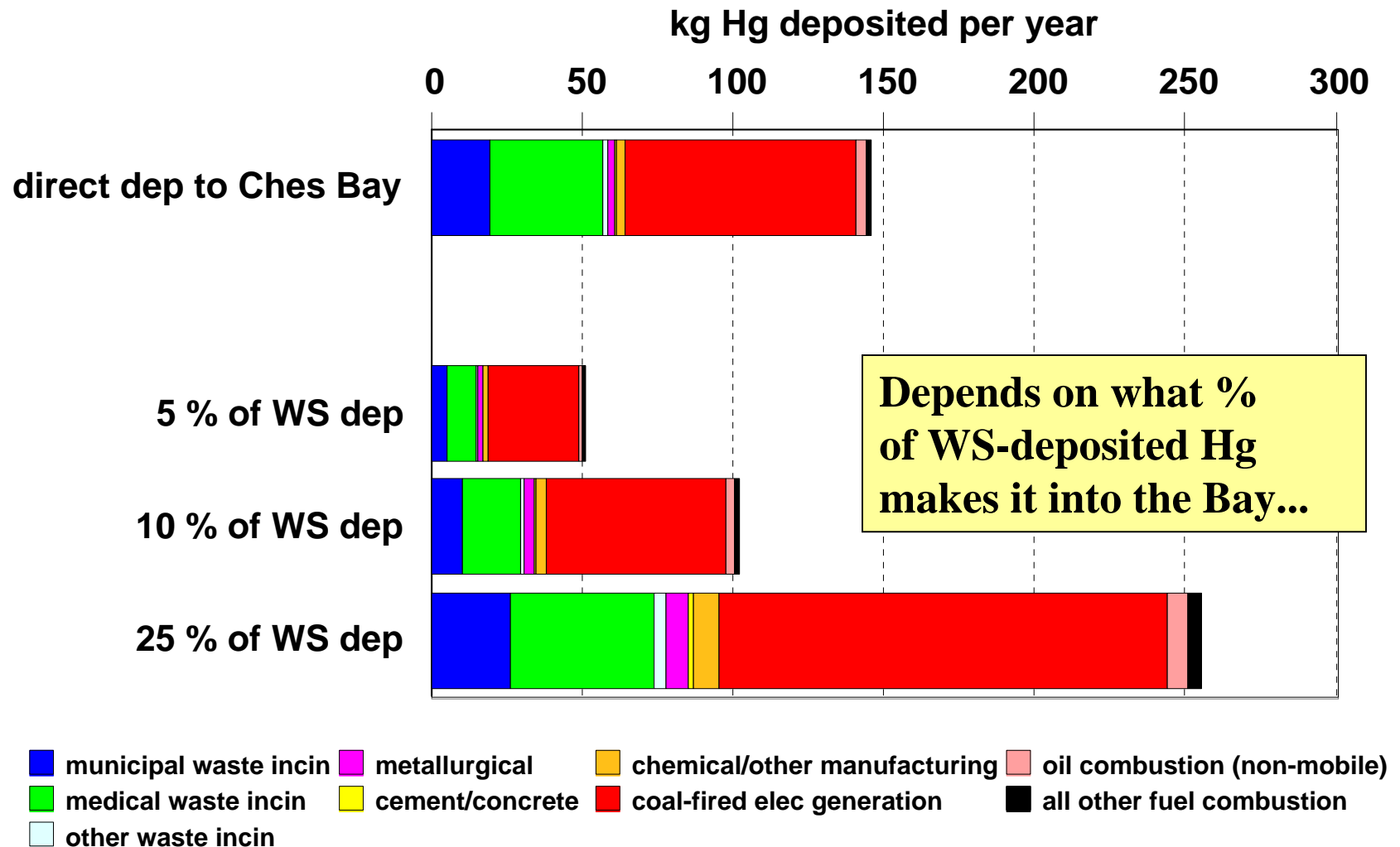
# Deposition to the Chesapeake Bay and to its Watershed (~1999) (logarithmic graph)








## Deposition to the Chesapeake Bay and to its Watershed (~1999) (linear graph)



# What is Relative Importance of Hg Deposited Directly to Chesapeake Bay Surface vs. Deposition to Watershed (?)

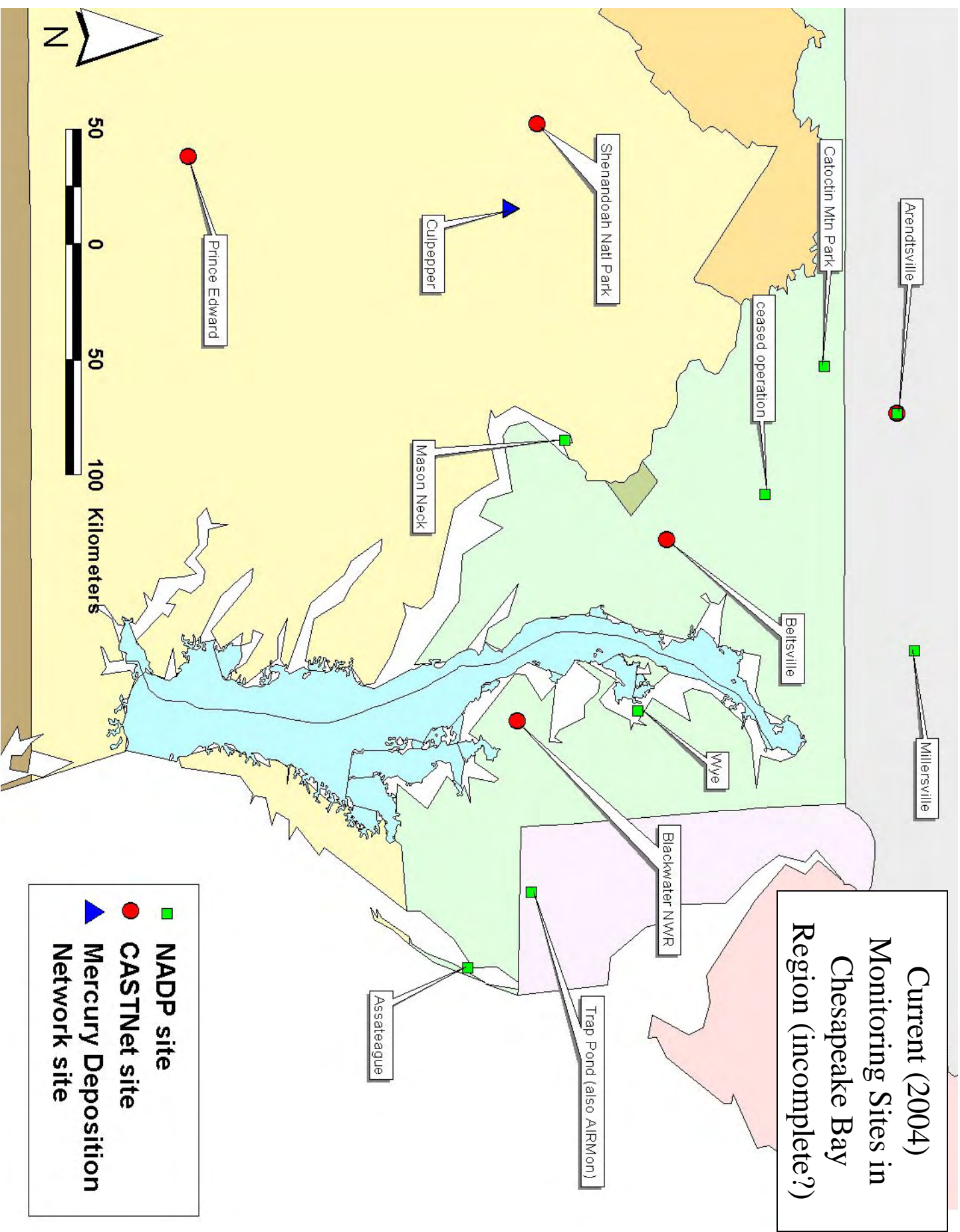


# Some Next Steps

-  Use more highly resolved meteorological data grid
-  Expand model domain to include global sources
-  Simulate natural emissions and re-emissions of previously deposited Hg
-  Additional model evaluation exercises ... more sites, more time periods, more variables (e.g., not just wet deposition).
-  Sensitivity analyses and examination of atmospheric Hg chemistry in the marine boundary layer and at upper elevations...



Current (2004)  
Monitoring Sites in  
Chesapeake Bay  
Region (incomplete?)





State of Utah

Department of  
Environmental Quality

Dianne R. Nielson, Ph.D.  
*Executive Director*

DIVISION OF AIR QUALITY  
Richard W. Sprott  
*Director*

OLENE S. WALKER  
*Governor*

GAYLE F. McKEACHNIE  
*Lieutenant Governor*

FILE COPY

DAQE-AN0327010-04

October 15, 2004

George W. Cross  
Intermountain Power Service Corporation  
850 West Brush Wellman Road  
Delta, Utah 84624-9522


Dear Mr. Cross:

Re: Approval Order: PSD Major Modification to Add New Unit 3 at Intermountain Power  
Generating Station, Millard County, Utah CDS-A, ATT, NSPS, HAPs, MACT, Title IV, Title V  
Major. Project Code: N0327-010

The attached document is the Approval Order (AO) for the above-referenced project.

Future correspondence on this Approval Order should include the engineer's name as well as the DAQE number as shown on the upper right-hand corner of this letter. Please direct any technical questions you may have on this project to Ms. Milka M. Radulovic. She may be reached at (801) 536-4232.

Sincerely,

  
Richard W. Sprott, Executive Secretary  
Utah Air Quality Board

RWS: MR: jc

cc: Central Utah Public Health Department  
Mike Owens, EPA Region VIII

**STATE OF UTAH**

**Department of Environmental Quality**

**Division of Air Quality**

**APPROVAL ORDER: PSD MAJOR MODIFICATION TO ADD  
NEW UNIT 3 AT INTERMOUNTAIN POWER GENERATING  
STATION**

**Prepared By: Milka M. Radulovic, Engineer  
(801) 536-4232**

**Email: [milkar@utah.gov](mailto:milkar@utah.gov)**

**APPROVAL ORDER NUMBER**

**DAQE-AN0327010-04**

**Date: October 15, 2004**

**Intermountain Power Service Corporation**

**Source Contact**

**George Cross**

**(435) 864-4414**

**Richard W. Sprott**

**Executive Secretary**

**Utah Air Quality Board**

## *Abstract*

*Intermountain Power Service Corporation (IPSC) currently operates the Intermountain Power Plant (IPP) located near the town of Delta, Utah. The existing plant has two drum-type, pulverized coal (PC)-fired boilers that provide steam to two power-generating units, designated as Unit 1 and Unit 2, each with nominal gross capacity of 950 MW. The Intermountain Power Service Corporation (IPSC) submitted a Notice of Intent to expand the IPP facility by adding one additional base load pulverized coal fired electricity generating Unit 3, designed at nominal 950-gross MW (900-net MW) with a dry bottom, tangentially fired or wall-fired boiler and associated equipment. The Unit 3 boiler will be equipped with wet flue gas desulphurization (WFGD), selective catalytic reduction (SCR), and baghouses for control of the various emissions.*

*This project is a major modification for the Prevention of Significant Deterioration (PSD) regulations. On site meteorological monitoring, air dispersion modeling, air quality impacts analysis including visibility and PSD class I and II impacts analysis, non-attainment boundary impact analysis, and a complete top-down Best Available Control Technology (BACT) review were completed and submitted by the IPSC as a part of their Notice of Intent (NOI). Also, an application for case-by-case maximum achievable control technology (MACT) determination for hazardous air pollutants (HAPs) was provided as a part of the NOI. Unit 3 is also subject to New Source Performance Standards under 40 Code of Federal Regulations (CFR) 60, Subparts A, Da and Y. Title IV and Title V of the 1990 Clean Air Act apply to this modification and the Title V permit shall be amended prior to the operation of the Unit 3. Unit 3 boiler will be classified Group I, Phase II under the Acid Rain Program. The increment analysis indicated that the amount of  $PM_{10}$  24-hour increment consumed by the proposed project would be less than 50% of the standard; therefore, approval under Utah Administrative Code R307-401-6 (3) from the Utah Air Quality Board was not required. The IPP will meet all primary and secondary National Ambient Air Quality Standards (NAAQS). The IPP will also meet Class I increments in the National Parks in southern Utah and Class II PSD increments in the vicinity of the plant. IPP Unit 3 will have no adverse effect on air quality related values (including visibility) on any Class I areas.*

*The IPP is located in Millard County, an attainment area for all criteria pollutants.*

*Estimated potential to emit totals from Unit 3, in tons per year, are as follows:  $PM_{10}$  (filterable) = 496.5,  $NO_x$  = 2,775,  $SO_2$  = 3,567.5, CO = 5,946, VOC = 107, HAPs = 199*

The project has been evaluated and found to be consistent with the requirements of the Utah Administrative Code Rule 307 (UAC R307). A public comment period was held in accordance with UAC R307-401-4 and comments were received. The comments were evaluated and the Approval Order was modified to incorporate those comments. This air quality Approval Order (AO) authorizes the project with the following conditions, and failure to comply with any of the conditions may constitute a violation of this order.

### **General Conditions:**

1. This Approval Order (AO) applies to the following company:

Site Location

Intermountain Power Service  
Corporation  
850 West Brush Wellman Road  
Delta, UT 84624-9522

Corporate Office Location

Intermountain Power Service  
Corporation  
850 W. Brush Wellman Road  
Delta, UT 84624

Phone Number: (435) 864-4414

Fax Number: (435) 864-6670

The equipment listed in this AO shall be operated at the following location:

850 West Brush Wellman Road, Delta, Millard County, Utah

Universal Transverse Mercator (UTM) Coordinate System: datum NAD27

4,374.4 kilometers Northing, 364.2 kilometers Easting, Zone 12

2. All definitions, terms, abbreviations, and references used in this AO conform to those used in the Utah Administrative Code (UAC) Rule 307 (R307) and Title 40 of the Code of Federal Regulations (40 CFR). Unless noted otherwise, references cited in these AO conditions refer to those rules.
3. The limits set forth in this AO shall not be exceeded without prior approval in accordance with R307-401.
4. Modifications to the equipment or processes approved by this AO that could affect the emissions covered by this AO must be reviewed and approved in accordance with R307-401-1.
5. All records referenced in this AO or in applicable NSPS and/or NESHAP and/or MACT standards, which are required to be kept by the owner/operator, shall be made available to the Executive Secretary or Executive Secretary's representative upon request, and the records shall include the five-year period prior to the date of the request. Records shall be kept for the following minimum periods:
  - A. Used oil consumption Five years
  - B. Emission inventories Five years from the due date of each statement or until the next inventory is due, whichever is longer.
  - C. All other records Five years
6. Intermountain Power Service Corporation (IPSC) shall install and operate the nominal 950 gross-MW power generating Unit 3 with dry-bottom pulverized coal fired boiler and modified equipment associated with Unit 3, as defined by this AO, in accordance with the terms and conditions of this AO, which was written pursuant to IPSC's Notice of Intent submitted to the Division of Air Quality (DAQ) on December 16, 2002 and significant additional information provided throughout the process.
7. The approved installations shall consist of the following equipment or equivalent\*:

- A. Unit 3 Dry-bottom Pulverized Coal Fired Boiler for base load operation with Overfire Air Ports System
  - Maximum Heat Input Rate:  $9050 \times 10^6$  Btu/hr
  - Type of Burner: Ultra Low NO<sub>x</sub> Burners or equivalent
- B. Unit 3 Main Boiler Stack
  - Stack Height: At least 712 feet, as measured from ground level at the base of the stack.
- C. Unit 3 Main Boiler Control Equipment:
  - C.1 Boiler Stack Fabric Filter Baghouse
  - C.2 Wet Limestone Flue Gas Desulfurization System (WFGD) built in redundancy
  - C.3 Selective Catalytic Reduction System with ammonia injection
- D. Two Unit 3 Cooling Towers, 3A and 3B, equipped with mechanical Mist Eliminators rated at 0.0005 percent circulating water drift loss.
- E. Unit 3 Coal Handling:
  - E.1 Modification of existing conveyors: higher capacity motors on Belts 7 and 8, Belts 9A/9B, 15A/15B expanded to 48" wide;
  - E.2 New Unit 3 36" wide Conveyors-16A/16B, 17A/17/B, en mass chain totally enclosed conveyors 301A/B, 302A/B, 303, 304, 305, and 306.
  - E.3 New Coal Transfer Building #5 with Dust Collector EP-127.
  - E.4 New Coal East Storage Silos 301, 302, 303, 304, and Coal East Storage Silo Bay Dust Collector EP-128.
  - E.5 New Coal West Storage Silos 305, 306, 307, 308 and Coal West Storage Silo Bay Dust Collector EP-129.
- F. Unit 3 Fly Ash Handling Equipment: To convey Fly Ash from the fabric filter to the storage silo:
  - F.1 Fly Ash Storage Silo 1C with Sealed Loading Spout Vent Dust Collector EP-171
  - F.2 Fly Ash Storage Silo 1C with Vent Dust Collector EP-172
- G. Unit 3 Bottom Ash Handling System to convey bottom ash from boiler to storage area.
- H. Unit 3 Limestone Handling System for WFGD system

- I. Unit 3 WFGD Sludge Handling System
- J. Existing Auxiliary Boiler Modification:  
Installation of an extension on each boiler stack so that each stack height is at least 72 feet, as measured from the ground level at the base of the stack.
- K. Unit 3 Water Treatment Plant, Steam System, Turbine generator, and Air heaters\*\*

\* Equivalency shall be determined by the Executive Secretary.

\*\* This equipment is listed for informational purposes only. There are no emissions from this equipment.

8. Intermountain Power Service Corporation shall notify the Executive Secretary in writing when the installation of the equipment listed in Condition #7 has been completed and is operational, as an initial compliance inspection is required. To insure proper credit when notifying the Executive Secretary, send your correspondence to the Executive Secretary, attn: Compliance Section.

If construction and/or installation has not been completed within eighteen months from the date of this AO, the Executive Secretary shall be notified in writing on the status of the construction and/or installation. At that time, the Executive Secretary shall require documentation of the continuous construction and/or installation of the operation and may revoke the AO in accordance with R307-401-11.

## Limitations and Tests Procedures

9. Emissions to the atmosphere from the indicated emission point(s) shall not exceed the following rates and concentrations:

Source: Unit 3 Main Boiler Stack, BACT/MACT		
Pollutant	Emission Rate (lb/MMBtu)	Averaging Period
SO <sub>2</sub>	0.10	24-hour block average
SO <sub>2</sub>	0.09	30-day rolling average
NO <sub>x</sub>	0.07	30-day rolling average
PM <sub>10</sub> (filterable)	0.012	3-test run average
PM (filterable)	0.013	3-test run average
CO	0.15	30-day rolling average
VOC	0.0027	3- test run average
H <sub>2</sub> SO <sub>4</sub>	0.0044	24-hour block average
Fluorides/HF	0.0005	3- test run average
Lead	0.00002	3- test run average
Hg- bituminous coal*	6 x 10 <sup>-6</sup> lb/ MWhr	12-month rolling average
Hg- subbituminous coal*	20 x 10 <sup>-6</sup> lb/ MWhr	12-month rolling average

Source: Unit 3 Main Boiler Stack, Air Quality Modeling		
Pollutant	Emission Rate (lb/hr)	Averaging Period
SO <sub>2</sub>	1,357.5	3-hour block average
NO <sub>x</sub>	633.5	24-hour block average
PM <sub>10</sub> (filterable+condensable)	221	24-hour block average**
CO	3,000	8-hour block average
HCL	38.13 lb/hr	3-test run average

\*If a blend of bituminous and subbituminous coals is used, the Hg emission limitation for the blend will be determined by 40 CFR 63.9990(a)(5) (Proposed Rules, Federal Register, Vol. 69, No. 20, January 30, 2004, pages 4720-4721).

\*\*Based on a 24-hour test run or any method approved by the Executive Secretary, which will provide 24-hour data.

24-hour block means the period of time between 12:01a.m. and 12:00 midnight.

8-hour block average means eight consecutive hours.

10. Stack testing to show compliance with the emission limitations stated in the above condition shall be performed as specified below:

A.	<u>Emissions Point</u>	<u>Pollutant</u>	<u>Testing Status</u>	<u>Test Frequency</u>
	Unit 3 Main Boiler Stack	PM <sub>10</sub> (f)/PM <sub>10</sub> (f+c)	Initial.....	Annual
		PM (f) .....	Initial.....	Annual**
		SO <sub>2</sub> .....	Initial.....	CEM
		NO <sub>x</sub> .....	Initial.....	CEM
		CO .....	Initial.....	CEM*
		H <sub>2</sub> SO <sub>4</sub> .....	Initial.....	Annual
		VOC .....	Initial.....	Annual
		Fluorides/HF.....	Initial.....	60-months
		Lead.....	Initial.....	60-months
		HCl .....	Initial.....	60-months
		Hg .....	Initial.....	Hg CEM***

f-filterable; c-condensable

\*or may use CEM equivalent, such as parametric monitoring that may be approved by the Executive Secretary

\*\*or parametric monitoring that may be approved by the Executive Secretary

\*\*\* 40 CFR 60, Appendix B, Performance Specification 12a (CEM) (Proposed Rules, Federal Register, Vol. 69, No. 20, January 30, 2004, page 4744) or 40 CFR 63, Appendix B, Method 324 (Sorbent Trap Sampling) (Proposed Rules, Federal Register, Vol. 69, No. 20, January 30, 2004, page 4736) or other testing methods that may be approved.

- B. Testing Status (To be applied to the source listed above)

Initial: Initial compliance testing is required. The initial test date shall be performed as soon as possible and in no case later than 180 days after the start up of a new emission source.



Annual: Test at least every year. The Executive Secretary may require testing at any time.

60-months: Test at least every five years. The Executive Secretary may require testing at any time.

CEM: After the initial compliance test, compliance shall be demonstrated through use of a Continuous Emissions Monitoring System (CEMs) as outlined in Condition below. The Executive Secretary may require testing at any time.

C. Notification

The Executive Secretary shall be notified at least 30 days prior to conducting any required emission testing. A source test protocol shall be submitted to DAQ when the testing notification is submitted to the Executive Secretary.

The source test protocol shall be approved by the Executive Secretary prior to performing the test(s). The source test protocol shall outline the proposed test methodologies, stack to be tested, and procedures to be used. A pretest conference shall be held, if directed by the Executive Secretary.

D. Sample Location

The emission point shall be designed to conform to the requirements of 40 CFR 60, Appendix A, Method 1, or other methods as approved by the Executive Secretary. An Occupational Safety and Health Administration (OSHA) or Mine Safety and Health Administration (MSHA) approved access shall be provided to the test location.

E. Volumetric Flow Rate

40 CFR 60, Appendix A, Method 2 or other approved methods.

F. PM/PM<sub>10</sub>

For stacks in which no liquid drops are present, the following methods shall be used: 40 CFR 51, Appendix M, Methods 201, 201A, or other approved methods. The back half condensibles shall also be tested using the method 202 or other approved methods. All particulate captured shall be considered PM<sub>10</sub>.

For stacks in which liquid drops are present, methods to eliminate the liquid drops should be explored. If no reasonable method to eliminate the drops exists (or for PM determination), then the following methods shall be used: 40 CFR 60, Appendix A, Method 5, 5A, 5B, or 5D, or as appropriate, or other approved methods. The back half condensibles shall also be tested using the Method 202 or other approved methods. The portion of the front half of the catch considered PM<sub>10</sub> shall be based on information in Appendix B of the fifth edition of the EPA document, AP-42, or other data acceptable to the Executive Secretary.

The back half condensibles shall not be used for compliance demonstration for PM (filterable) limit but shall be used for inventory purposes.

For determination of compliance with PM<sub>10</sub> limit, both the front and backhalf catches shall be used.

G. Sulfur Dioxide (SO<sub>2</sub>)

40 CFR 60, Appendix A, Method 6, 6A, 6B, 6C or other approved methods

H. Nitrogen Oxides (NO<sub>x</sub>)

40 CFR 60, Appendix A, Method 7, 7A, 7B, 7C, 7D, 7E or other approved methods

I. Sulfuric Acid Mist (H<sub>2</sub>SO<sub>4</sub>)

40 CFR 60, Appendix A, Method 8, 8A or other approved methods

J. Carbon Monoxide (CO)

40 CFR 60, Appendix A, Method 10, or other approved methods.

K. Volatile Organic Compounds (VOCs)

40 CFR 60, Appendix A, Method 25 or 25A or other approved methods.

L. Hydrogen chloride (HCl)

40 CFR 60, Appendix A, Method 26 or 26A or other approved methods.

M. Fluorides/Hydrogen fluoride (HF-hydrofluoric acid)

40 CFR 60, Appendix A, Method 26 or 26A or other approved methods.

N. Lead

40 CFR 60, Appendix A, Method 12 or other approved methods.

O. Mercury

ASTM Method D6784-02 or 40 CFR 60, Appendix A, Method 29 or other approved methods.

P. Calculations for Testing Results

To determine mass emission rates (lb/hr, etc.) the pollutant concentration as determined by the appropriate methods above shall be multiplied by the volumetric flow rate and any necessary conversion factors determined by the Executive Secretary, to give the results in the specified units of the emission limitation.

Q. New Source Operation

For a new source/emission point, the production rate during all compliance testing shall be no less than 90% of the production rate listed in this AO. If the maximum AO allowable production rate has not been achieved at the time of the test, the following procedure shall be followed:

1. Testing shall be at no less than 90% of the production rate achieved to date.
2. If the test is passed, the new maximum allowable production rate shall be 110% of the tested achieved rate, but not more than the maximum allowable production rate. This new allowable maximum production rate shall remain in effect until successfully tested at a higher rate.
3. The owner/operator shall request a higher production rate when necessary. Testing at no less than 90% of the higher rate shall be conducted. A new maximum production rate (110% of the new rate) will then be allowed if the test is successful. This process may be repeated until the maximum AO production rate is achieved.

R. Existing Source Operation

For an existing source/emission point, the production rate during all compliance testing shall be no less than 90% of the maximum production achieved in the previous three (3) years

11. Differential pressure range at the indicated points shall be within the following values

Unit 3 Dust Collectors

<u>Source</u>	<u>Differential pressure range across the dust collector</u> (Inches of water gage)
Fly Ash Storage Silo 1C Loading Spout Vent (EP-171) .....	0.5 to 12*
Fly Ash Storage Silo 1D Vent (EP-172).....	0.5 to 12*
Coal Transfers Building #5 Vent (EP-127) .....	0.5 to 12*
Coal East Storage Silo Bay (EP-128) .....	0.5 to 12*
Coal West Storage Silo Bay (EP-129) .....	0.5 to 12*

\*If differential pressure is less than 2 inches or greater than 10 inches, work orders will be written to investigate. Dust collector may run in the 0.5 to 2 or 10 to 12 range if reason is known. Recording of the reading is required on a monthly basis. The instrument shall be calibrated against a primary standard annually. Preventive maintenance shall be done quarterly on each baghouse.

12. Visible emissions from the emission points covered under this AO shall not exceed the following values:

- A. All baghouses (including the Unit 3 main boiler stack) - 10% opacity

B. All other points - 20% opacity

Opacity observations of emissions from stationary sources shall be conducted according to 40 CFR 60, Appendix A, Method 9. Visible emissions from intermittent sources shall use proposed Method 203 A, B, and C, as applicable. For sources that are subject to NSPS, opacity shall be determined by conducting observations in accordance with 40 CFR 60.11(b) and 40 CFR 60, Appendix A, Method 9.

13. IPSC shall abide by a boiler manufacturer written instructions and/or written procedures developed and maintained by IPSC for the Unit 3 main boiler startup, shutdown, and malfunction periods. These instructions and/or written procedures shall be available to the Executive Secretary or Executive Secretary's representative upon request.
14. The following Unit 3 boiler heat rate and consumption limits shall not be exceeded:
  - A. 9050 million British Thermal Units (MMBtu) per hour full load heat input rate for Unit 3 boiler, using Higher Heating Value HHV of the fuel.
  - B. 3,541,248 tons of coal burned per rolling 12-month period

Records of consumption/heat rate input shall be kept for all periods when the plant is in operation. The records of consumption/production shall be kept on a daily basis.

15. Unit 1 & 2 emergency generator located at (source ID102) shall be tested for maintenance only during the periods between 6:00AM and 6:00 PM. Records of the time, date, and duration of emergency generator testing shall be determined by supervisor monitoring and maintaining of an operations log.

### **Roads and Fugitive Dust**

16. The facility shall abide by all applicable requirements of R307-205 for Fugitive Emission and Fugitive Dust sources.
17. IPSC shall abide by a fugitive dust control plan acceptable to the Executive Secretary for the control of all dust sources associated with the addition of Unit 3 at the Intermountain Power Generation site. IPSC shall submit a fugitive dust control plan to the Executive Secretary, Attention: Compliance Section, for approval within 90 days of the date of this AO. This plan shall contain sufficient controls to prevent an increase in PM<sub>10</sub> emissions above those modeled for this AO. In addition, as a minimum the following control measures shall be included in the plan:
  - a. Vacuum street sweeping for paved haul roads;
  - b. Chemical stabilization for unpaved haul roads;
  - c. Water sprays for conditioned sludge handling;
  - d. Wet suppression with chemicals for long term reserve and emergency coal storage piles;
  - e. Surfactants and compaction for active coal storage piles and their maintenance;
  - f. Telescopic chute, enclosures and surfactants for coal handling.

Any changes of the conditions established in the fugitive dust control plan must be approved by the Executive Secretary.

18. Visible fugitive dust emissions from Unit 3 haul-road traffic and mobile equipment in operational areas shall not exceed 20% opacity. Visible emissions determinations for traffic sources shall use procedures similar to Method 9. The normal requirement for observations to be made at 15-second intervals over a six-minute period, however, shall not apply. Six points, distributed along the length of the haul road or in the operational area, shall be chosen by the Executive Secretary or the Executive Secretary's representative. An opacity reading shall be made at each point when a vehicle passes the selected points. Opacity readings shall be made  $\frac{1}{2}$  vehicle length or greater behind the vehicle and at approximately  $\frac{1}{2}$  the height of the vehicle or greater. The accumulated six readings shall be averaged for the compliance value.

### **Fuels**

19. The owner/operator shall use either bituminous or blend of bituminous and up to thirty percent subbituminous coals as a primary fuel, blended to meet emission performance standards. The owner/operator shall use fuel oil during the startups, shutdowns, maintenance, upset conditions and flame stabilization in the Unit 3  $9050 \times 10^6$  Btu/hr boiler. The owner/operator may blend self-generated used oil with coal at the active coal pile reclaim structure providing record that self-generated used oil has not been mixed with hazardous waste.

20. The sulfur content of any fuel oil burned shall not exceed:

$0.85 \text{ lb per } 10^6 \text{ Btu heat input for fuel used in the Unit 3 } 9050 \times 10^6 \text{ Btu/hr boiler}$

The sulfur content shall comply with all applicable sections of R307-203. Methods for determining sulfur content of coal shall be those methods of the American Society for Testing and Materials

- A. For determining sulfur content in coal, ASTM Methods D3177-75 or D4239-85 are to be used.
- B. For determining the gross calorific (or Btu) content of coal, ASTM Methods D2015-77 or D3286-85 are to be used.
- C. The sulfur content of fuel oil shall be determined by ASTM Method D-4294-89 or approved equivalent. Certification of fuel oil shall either be by SPC's own testing or test reports from the fuel oil marketer.

### **Federal Limitations and Requirements**

21. In addition to the requirements of this AO, all applicable provisions of 40 CFR 60, New Source Performance Standards (NSPS) Subpart A, 40 CFR 60.1 to 60.18, Subpart Da, 40 CFR 60.40a to 60.49a (Standards of Performance for Electric Utility Steam Generating Units for Which Construction in Commenced After September 18, 1978), Y, 40 CFR 60.250 to 60.254 (Standards of Performance for Coal Preparation Plants), and 40 CFR 64 (Compliance Assurance Monitoring for Major Stationary Sources) apply to this installation.

22. In addition to the requirements of this AO, all applicable provisions of 40 CFR Part 72, 73, 75, 76, 77, and 78 - Federal regulations for the Acid Rain Program under Clean Air Act Title IV apply to this installation.

### **Monitoring - General Process**

23. The owner/operator shall install, calibrate, maintain, and operate a continuous emissions monitoring system (CEMs) on the main boilers stacks and SO<sub>2</sub> removal scrubbers inlets. The owner/operator shall record the output of the system, for measuring the opacity, SO<sub>2</sub>, CO, and NO<sub>x</sub> emissions. The monitoring system shall comply with all applicable sections of R307-170, UAC; and 40 CFR 60, Appendix B.

All continuous emissions monitoring devices as required in federal regulations and state rules shall be installed and operational prior to placing the affected source in operation.

Except for system breakdown, repairs, calibration checks, and zero and span adjustments required under paragraph (d) 40 CFR 60.13, the owner/operator of an affected source shall continuously operate all required continuous monitoring devices and shall meet minimum frequency of operation requirements as outlined in 40 CFR 60.13 and Section UAC R307-170.

### **Records & Miscellaneous**

24. The condition below applies to IPSC during periods of scheduled maintenance, startup, or shutdown unless periods of scheduled maintenance, startup, or shutdown are addressed by the Utah Administrative Code.

Excess emissions due to scheduled maintenance, startup, or shutdown shall constitute a violation. However, the incident may qualify for an affirmative defense as outlined below. If IPSC has emissions in excess of an applicable emission limitation due to scheduled maintenance, startup, or shutdown they may have an affirmative defense to a civil, administrative, or other proceeding, other than an action seeking injunctive relief, and they could be excused from penalties if they have demonstrated all of the following:

- A. Excess emissions that occurred during scheduled maintenance, startup or shutdown were short and infrequent and could not have been prevented through careful planning and design consistent with good industry practices;
- B. The excess emissions were not part of a recurring pattern indicating inadequate design, operation, or maintenance;
- C. If the excess emissions were caused by an intentional bypass of control equipment, then the bypass was unavoidable to prevent loss of life, personal injury, or severe property damage;
- D. At all times, the facility was operated in a manner consistent with good practice for minimizing emissions such as manufacturers' recommendations and general industry adopted practices;
- E. The frequency and duration of operation in scheduled maintenance, startup, or shutdown mode were minimized to the extent practicable;

- F. All practicable steps were taken to minimize the impact of the excess emissions on ambient air quality;
- G. All emission monitoring systems were kept in operation if possible;
- H. The owner or operator's actions during the period of excess emissions were documented by contemporaneous operating logs or other relevant evidence;
- I. The owner or operator provided notice in accordance with R307-107-2, if required; and
- J. The excess emissions did not cause or contribute to an exceedance of the NAAQS or PSD increments.

IPSC shall report to the Executive Secretary any excess emissions due to scheduled maintenance, startup, or shutdown with a duration of 2 hours or longer as outlined below. Failure to comply with the following reporting requirements and procedures shall preclude the use of the affirmative defense.

- A. Initial Report. IPSC shall notify the Executive Secretary by telephone or facsimile within 3 hours of the time they first learn of the occurrence of excess emissions of a duration of 2 hours or longer. The notification shall include the information listed in paragraph (b) below to the extent that information is available at the time of the initial report.
- B. Detailed Report. In the case of excess emissions with a duration of two hours or longer, IPSC shall provide the Executive Secretary with a detailed excess emissions report in writing within 7 calendar days of the time the initial report was due. The report shall include the following:
  - (i) The company name and location, and the identity of each stack or other emission point where the excess emissions occurred;
  - (ii) The magnitude of the excess emissions expressed in the units of the applicable emission limitation and the operating data and calculations used in determining the magnitude of the excess emissions;
  - (iii) The date, starting time, and duration or expected duration of the excess emissions to include indicating who first identified the excess emissions and when;
  - (iv) The identity of the equipment from which the excess emissions emanated;
  - (v) A specific explanation of the cause and nature of the emissions;
  - (vi) The steps taken to remedy the excess emissions, and the steps taken or planned to prevent the recurrence of the excess emissions;
  - (vii) The steps that were or are being taken to limit the excess emissions; and
  - (viii) The steps taken to comply with any applicable procedures governing operations during periods of excess emissions.

25. At all times, including periods of startup, shutdown, and malfunction, owners and operators shall, to the extent practicable, maintain and operate any equipment approved under this Approval Order including associated air pollution control equipment in a manner consistent with good air pollution control practice for minimizing emissions. Determination of whether acceptable operating and maintenance procedures are being used will be based on information available to the Executive Secretary which may include, but is not limited to, monitoring results, opacity observations, review of operating and maintenance procedures, and inspection of the source. All maintenance performed on equipment authorized by this AO shall be recorded.
26. The owner/operator shall comply with R307-150 Series. Inventories, Testing and Monitoring.
27. The owner/operator shall comply with R307-107. General Requirements: Unavoidable Breakdowns.

The Executive Secretary shall be notified in writing if the company is sold or changes its name.

Under R307-150-1, the Executive Secretary may require a source to submit an emission inventory for any full or partial year on reasonable notice.

This AO in no way releases the owner or operator from any liability for compliance with all other applicable federal, state, and local regulations including R307.

A copy of the rules, regulations and/or attachments addressed in this AO may be obtained by contacting the Division of Air Quality. The Utah Administrative Code R307 rules used by DAQ, the Notice of Intent (NOI) guide, and other air quality documents and forms may also be obtained on the Internet at the following web site: <http://www.airquality.utah.gov/>

The annual emissions estimations below are for the purpose of determining the applicability of Prevention of Significant Deterioration, non-attainment area, maintenance area, and Title V source requirements of the R307. They are not to be used for determining compliance.

The Potential to Emit (PTE) emissions for the entire Unit 3 operations are currently calculated at the following values:

	<u>Pollutant</u>	<u>Tons/yr</u>
A.	PM <sub>10</sub> (filterable) .....	496.5
B.	SO <sub>2</sub> .....	3,567.5
C.	NO <sub>x</sub> .....	2775
D.	CO .....	5946
E.	VOC .....	107
F.	H <sub>2</sub> SO <sub>4</sub> .....	174
G.	Lead .....	0.79
H.	Total Reduced Sulfur .....	29
I.	Reduced Sulfur Compounds .....	29



J. HAPs

Mercury.....0.0413

Hydrochloric Acid (HCL).....167.01

Fluorides/HF .....20

Total HAPs ..... 199

Approved By:



Richard W. Sprott, Executive Secretary  
Utah Air Quality Board



# *COMMONWEALTH of VIRGINIA*

## *DEPARTMENT OF ENVIRONMENTAL QUALITY* SOUTHWEST REGIONAL OFFICE

L. Preston Bryant, Jr.  
Secretary of Natural Resources

355 Deadmore Street, P.O. Box 1688, Abingdon, Virginia 24212  
(276) 676-4800 Fax (276) 676-4899  
[www.deq.virginia.gov](http://www.deq.virginia.gov)

David K. Paylor  
Director

Dallas R. Sizemore  
Regional Director

June 30, 2008

Mr. James K. Martin  
Vice President  
Virginia Electric and Power Company  
5000 Dominion Boulevard  
Glen Allen, Virginia 23060

Location: Wise County  
Registration No. 11526

Dear Mr. Martin:

Attached is a permit to construct and operate a coal-fired steam electric generating plant in accordance with the provisions of 9 VAC 5-80 Article 7 of the Virginia State Air Pollution Control Board (Board) Regulations for the Control and Abatement of Air Pollution.

At its meeting on June 25, 2008, the Board directed the Department of Environmental Quality (DEQ) to make the changes specified in their amendments approved at the meeting and issue this final permit. A summary of the Board-directed changes are as follows:

1. Decrease the emission limit for Mercury (Hg) to 0.00000088 pounds per megawatt-hour (lb/MWhr) and remove the pound per year (lb/yr) limit. DEQ understands the Board took this action based on sorbent trap stack test results from the Reliant Energy Seward power plant in Pennsylvania that reflect the highest individual test run at Seward (0.03 pound per trillion British Thermal Unit (lb/TBtu), multiplied by a safety factor of 3. The Board directed DEQ to convert the input-based number derived from that calculation (0.09 lb/TBtu) to an out-put based number, which will be the limit used for compliance purposes. The conversion factor used by the DEQ was  $9.8 \times 10^{-6}$  lb/MWhr per lb/TBtu. The 0.09 lb/TBtu is retained in the permit parenthetically as the basis for the lb/MWhr limit.
2. Decrease the emissions limit for hydrogen chloride (HCl) to 0.0029 pound per million Btu (lb/MMBtu). DEQ understands the Board took this action to reflect the most

stringent limit for HCL identified in DEQ's review of permits for recently constructed utility coal boilers.

3. Decrease the emissions limit for carbon monoxide (CO) to 0.10 lb/MMBtu. DEQ understands the Board took this action to reflect the most stringent limit for CO identified in DEQ's review of permits for recently constructed utility coal boilers.

This permit contains legally enforceable conditions. Failure to comply may result in a Notice of Violation and/or civil charges. Please read all permit conditions carefully.

In the course of evaluating the application and arriving at a final decision to approve the project, the DEQ deemed the application complete on February 27, 2008, and solicited written public comments by placing a newspaper advertisement in the *Bristol Herald Courier*, *Kingsport Times-News*, and the *Clinch Valley Times* on March 4, 2008. A public hearing was held on April 3, 2008 in St. Paul, Virginia. The required comment period provided by 9 VAC 5-80-1460 E expired on April 18, 2008.

This permit approval to construct and operate shall not relieve Virginia Electric and Power Company of the responsibility to comply with all other local, state, and federal permit regulations.

The Board's Regulations as contained in Title 9 of the Virginia Administrative Code 5-170-200 provide that you may request a formal hearing from this case decision by filing a petition with the Board within 30 days after this case decision notice was mailed or delivered to you. 9 VAC 5-170-200 provides that you may request direct consideration of the decision by the Board if the Director of the DEQ made the decision. Please consult the relevant regulations for additional requirements for such requests.

As provided by Rule 2A:2 of the Supreme Court of Virginia, you have 30 days from the date you actually received this permit or the date on which it was mailed to you, whichever occurred first, within which to initiate an appeal of this decision by filing a Notice of Appeal with:

David K. Paylor, Director  
Department of Environmental Quality  
P. O. Box 1105  
Richmond, VA 23218

If this permit was delivered to you by mail, three days are added to the thirty-day period in which to file an appeal. Please refer to Part Two A of the Rules of the Supreme Court of Virginia for information on the required content of the Notice of Appeal and for additional requirements governing appeals from decisions of administrative agencies.

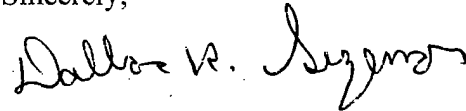
Mr. James K. Martin

June 30, 2008

Page 3

If you have any questions concerning this permit, please contact the regional office at (276) 676-4800.

Sincerely,

A handwritten signature in black ink, appearing to read "Dallas R. Sizemore".

Dallas R. Sizemore  
Regional Director

Attachments:      Permit  
                         NSPS, Subpart Da  
                         NESHAPS, Subparts A and B  
                         Source Testing Report Format

cc:      Director, OAPP (electronic file submission)  
         Manager, Data Analysis (electronic file submission)  
         Chief, Air Enforcement Branch (3AP13), U.S. EPA, Region III  
         Manager/Inspector, Air Compliance



# *COMMONWEALTH of VIRGINIA*

## *DEPARTMENT OF ENVIRONMENTAL QUALITY* SOUTHWEST REGIONAL OFFICE

L. Preston Bryant, Jr.  
Secretary of Natural Resources

355 Deadmore Street, P.O. Box 1688, Abingdon, Virginia 24212  
(276) 676-4800 Fax (276) 676-4899  
[www.deq.virginia.gov](http://www.deq.virginia.gov)

David K. Paylor  
Director

Dallas R. Sizemore  
Regional Director

### **ARTICLE 7 (40 CFR Part 63 112(g)) CASE-BY-CASE MACT PERMIT STATIONARY SOURCE PERMIT TO CONSTRUCT AND OPERATE**

In compliance with the Federal Clean Air Act and the Commonwealth of Virginia  
Regulations for the Control and Abatement of Air Pollution,

Virginia Electric and Power Company  
5000 Dominion Boulevard  
Glen Allen, Virginia 23060  
Registration No.: 11526

is authorized to construct and operate

two circulating fluidized bed (CFB) boilers each rated at  $3,132 \times 10^6$  Btu/hr (MMBtu/hr) with a combined 668 megawatts (MW)  
gross electrical output

located at

Alternate Route 58, Virginia City, Wise County, Virginia

in accordance with the conditions of this permit.

Approved on June 30, 2008.

A handwritten signature in black ink, reading "Dallas R. Sizemore".

Dallas R. Sizemore  
Regional Director

Permit consists of 26 pages and Attachment.  
Permit Conditions 1 to 50.  
Attachment: Mercury Monitoring Provisions

## **INTRODUCTION**

This permit approval is based on the permit application dated February 15, 2008; as updated February 25, 2008 with emission calculations and February 27, 2008 with coal analyses and a replacement page 16 of the application. Any changes in the permit application specifications or any existing facilities which alter the impact of the facility on air quality may require a permit. Failure to obtain such a permit prior to construction may result in enforcement action.

Words or terms used in this permit shall have meanings as provided in 9 VAC 5-10-20 and 9 VAC 5-80-1410 of the State Air Pollution Control Board Regulations for the Control and Abatement of Air Pollution. The regulatory reference or authority for each condition is listed in parentheses () after each condition.

Annual requirements to fulfill legal obligations to maintain current stationary source emissions data will necessitate a prompt response by the permittee to requests by the DEQ or the Board for information to include, as appropriate: process and production data; changes in control equipment; and operating schedules. Such requests for information from the DEQ will either be in writing or by personal contact.

The availability of information submitted to the DEQ or the Board will be governed by applicable provisions of the Freedom of Information Act, §§ 2.2-3700 through 2.2-3714 of the Code of Virginia, § 10.1-1314 (addressing information provided to the Board) of the Code of Virginia, and 9 VAC 5-170-60 of the State Air Pollution Control Board Regulations. Information provided to federal officials is subject to appropriate federal law and regulations governing confidentiality of such information.

## **PROCESS REQUIREMENTS**

1. **Equipment List** - Equipment at this facility consists of the following:

<b>Equipment to be Constructed</b>			
<b>Reference No.</b>	<b>Equipment Description</b>	<b>Rated Capacity</b>	<b>Federal Emission Standards</b>
CFB1 and CFB2	Two circulating fluidized bed (CFB) boilers	$3,132 \times 10^6$ Btu/hr (MMBtu/hr) each with a combined 668 megawatts (MW) gross electrical output	Case-by-Case MACT 112(g)

Specifications included in the permit under this condition are for informational purposes only and do not form enforceable terms or conditions of the permit.  
(9 VAC 5-80-1470 D 3)

2. **Emission Controls** – Particulate hazardous air pollutant emissions from each CFB boiler shall be controlled by a fabric filter baghouse. Each fabric filter baghouse shall be provided with adequate access for inspection.  
(9 VAC 5-80-1470 and 40 CFR 63.43(g))

3. **Emission Controls** – Hydrogen chloride and hydrogen fluoride emissions from the CFB boilers shall be controlled by limestone injection into each boiler, a flue gas desulfurization system for each boiler, and a fabric filter baghouse for each boiler. Each limestone injection, flue gas desulfurization system and fabric filter baghouse shall be provided with adequate access for inspection. This condition applies at all times except during startup and shutdown of the CFB boilers.  
(9 VAC 5-80-1470 and 40 CFR 63.43(g))
4. **Emission Controls** – Volatile organic hazardous air pollutant emissions from the CFB boilers shall be controlled by good combustion practices, an activated carbon injection system for each boiler and a fabric filter baghouse for each boiler. Each boiler, activated carbon injection system, and fabric filter baghouse shall be provided with adequate access for inspection.  
(9 VAC 5-80-1470 and 40 CFR 63.43(g))
5. **Emission Controls** – Mercury emissions from the CFB boilers shall be controlled by a flue gas desulfurization system for each boiler, an activated carbon injection system for each boiler, and a fabric filter baghouse for each boiler. Each flue gas desulfurization system, activated carbon injection system, and fabric filter baghouse shall be provided with adequate access for inspection.  
(9 VAC 5-80-1470 and 40 CFR 63.43(g))
6. **Emissions Testing** – The CFB boilers shall be constructed so as to allow for emissions testing upon reasonable notice at any time, using appropriate methods. Upon request by DEQ, sampling ports, safe sampling platforms and access shall be provided at the appropriate locations.  
(9 VAC 5-80-1470, 9 VAC 5-50-30 F and 40 CFR 63.43(g))

### **OPERATING LIMITATIONS**

7. **Heat Input** – Heat input to each CFB boiler shall not exceed  $27,436,320 \times 10^6$  Btu per year, calculated monthly as the sum of each consecutive 12-month period. Compliance for the consecutive 12-month period shall be demonstrated monthly by adding the total for the most recently completed calendar month to the individual monthly totals for the preceding 11 months.  
(9 VAC 5-80-1470 and 40 CFR 63.43(g))
8. **Fuel** – The approved fuels for the CFB boilers are bituminous coal, coal refuse, wood/bark, distillate oil and diesel fuel. The fuels shall meet the following specifications:

COAL and COAL REFUSE:

Maximum sulfur content as-fired: 2.28% as determined  
by ASTM D3177, D4239, or a DEQ-approved equivalent method.

**COAL and COAL REFUSE:**

Maximum annual average sulfur content: 1.5% calculated  
monthly as the average of the previous 12-month period using results from weekly sampling  
and analysis required in Condition 9.

**DISTILLATE OIL** which meets the ASTM D396 specification for numbers 1 or 2 fuel oil:  
Maximum sulfur content per shipment: 0.0015%

**WOOD/BARK** excluding any wood which contains chemical treatments or has affixed  
thereto paint and/or finishing materials or paper or plastic laminates.

**DIESEL FUEL** which meets the ASTM D975 specification for numbers 1-D S15 or 2-D S15  
diesel fuel:  
Maximum sulfur content per shipment: 0.0015%

A change in the fuels may require a permit to modify and operate.  
(9 VAC 5-80-1470 and 40 CFR 63.43(g))

9. **Fuel Sampling and Analysis** – The permittee shall sample and analyze the fuel as fired in each CFB boiler for mercury, fluorides, chlorides, sulfur, and Btu content no less than once each calendar week using methods approved by the Director, Southwest Regional Office. Results of analyses shall be used in calculations to verify compliance with mercury, hydrogen fluoride, hydrogen chloride and sulfuric acid mist emission limits for the CFB boilers. A record of each analysis shall be maintained and shall include, at a minimum, content of each parameter, company and individual collecting the sample, identification of sampling method used, sample mass, number of samples, date sample collected, location of fuel when sample taken, date of analysis, company and individual conducting the analysis.  
(9 VAC 5-80-1470 and 40 CFR 63.43(g))
10. **Fuel Throughput** – The throughput of coal and coal refuse to each CFB boiler shall not exceed 1,760,760 tons per year calculated monthly as the sum of each consecutive 12-month period. Compliance for the consecutive 12-month period shall be demonstrated monthly by adding the total for the most recently completed calendar month to the individual monthly totals for the preceding 11 months.  
(9 VAC 5-80-1470 and 40 CFR 63.43(g))
11. **Fuel Throughput** – The throughput of wood/bark to each CFB boiler shall not exceed 685,000 tons per year calculated monthly as the sum of each consecutive 12-month period. Compliance for the consecutive 12-month period shall be demonstrated monthly by adding the total for the most recently completed calendar month to the individual monthly totals for the preceding 11 months.  
(9 VAC 5-80-1470 and 40 CFR 63.43(g))



12. **Fuel Certification** – The permittee shall obtain a certification from the fuel supplier with each shipment of coal, coal refuse, wood/bark, distillate oil and diesel fuel. Each fuel supplier certification shall include the following:
- The name of the fuel supplier;
  - The date on which the fuel was received;
  - The quantity of fuel delivered in the shipment;
  - A statement that the oil meets the ASTM D396 specification for fuel oil numbers 1 or 2, or ASTM D975 for diesel fuel numbers 1-D S15 or 2-D S15;
  - The sulfur content of the fuel, excluding wood/bark;
  - Documentation of sampling of the fuel indicating the location of the fuel when the sample was taken; and
  - The methods used to determine the sulfur content of the fuel.

The permittee shall submit a fuel shipment certification plan at least 60 days prior to facility startup for approval by the Director, Southwest Regional Office. Fuel sampling and analysis, independent of that used for certification, as may be periodically required or conducted by DEQ may be used to determine compliance with the fuel specifications stipulated in this permit. Exceedance of these specifications may be considered credible evidence of the exceedance of emission limits.

(9 VAC 5-80-1470, 9 VAC 5-50-410 and 40 CFR 63.43(g))

### **EMISSION LIMITS**

13. **Emission Limits** – Emissions from the operation of the CFB boilers shall not exceed the following limits:

	Each Boiler (lb/MMBtu)	Each Boiler (lb/hr) <sup>a</sup>	Combined Total (tons/yr)
Filterable Particulate Matter (PM)			246.92
3-hour average	0.010	31.32	
30-day rolling average	0.009		
Total PM-10 (filterable & condensable)			329.24
3-hour average	0.012	37.58	
Total PM-2.5 (filterable & condensable)			329.24 <sup>b</sup>
3-hour average	0.012 <sup>b</sup>	37.58 <sup>b</sup>	

	Each Boiler (lb/MMBtu)	Each Boiler (lb/hr) <sup>a</sup>	Combined Total (tons/yr)
Carbon Monoxide 30-day rolling average	0.10 <sup>c</sup>	313.2	2743.63
Volatile Organic Compounds 3-hour average	0.005	15.66	137.18
Hydrogen Fluoride 3-hour average	0.00047	1.47	12.90
Hydrogen Chloride 3-hour average	0.0029	9.08	79.54
Mercury	(lb/MWhr) 0.00000088 <sup>d</sup>	(0.090 lb/TBtu equivalent)	

<sup>a</sup> Compliance with the lb/hr limit is based on the averaging period indicated in the appropriate row.

<sup>b</sup> This permit may be changed in accordance with 9 VAC 5-80-1925, to reduce the emission limit based on results from stack testing as required in Condition 27 of this permit.

<sup>c</sup> Emission limit applies at loads equal to or greater than 75 percent of maximum load. Maximum load for each CFB boiler is considered to be 3,132 MMBtu/hr heat input. The emission limit for loads less than 75 percent is the 30-day load-weighted average expressed by the formula below. The emission limit for loads equal to or greater than 75 percent is fixed at 0.15 lb/MMBtu, however, this limit is factored into the 30-day load-weighted average for loads less than 75 percent. The permittee shall calculate the 30-day weighted average emission limit for loads less than 75 percent using the following formula:

$$EL_{CO\ 30d\ L} = \frac{\sum_{i=1}^n EL_i \times IR_i}{\sum_{i=1}^n IR_i}$$

where,

$EL_{CO\ 30d\ L}$  = 30-day weighted average carbon monoxide emission limit;  
lb/MMBtu

$EL_i$  = 0.15 lb/MMBtu for loads equal to or greater than 75 percent, or  
0.20 lb/MMBtu for loads less than 75 percent

$IR_i$  = the heat input rate corresponding to the incremental CEMS reading; MMBtu  
 $i$  = incremental CEMS reading having a non-zero heat input rate  
 $n$  = the number of incremental CEMS readings in the rolling 30-day period when there is a heat input rate in the load range

- <sup>d</sup> Compliance with the emission limit shall be based on the total mercury emissions from each CFB boiler contributed by each fuel burned during the compliance period and total MWhr contributed by each fuel burned during the compliance period. The permittee shall calculate the mercury emission rate in lb/MWhr for each calendar month of the year, using hourly mercury concentrations measured in accordance with Condition 18 and in conjunction with hourly stack gas volumetric flow rates measured in accordance with Condition 17, and hourly gross electrical outputs, determined in accordance with Condition 23. Compliance with the mercury emission limits shall be determined on a 12-month rolling average basis and using stack test data if stack testing is conducted during that month. Mercury emissions contributed by wood/bark and fuel oil combustion shall be calculated using emission factors or methods approved by the Director, Southwest Regional Office. Compliance with the applicable emission limit shall be determined on a 12-month rolling average basis.

Annual emissions are derived from the estimated overall emission contribution from operating limits including startup and shutdown. Exceedance of the operating limits may be considered credible evidence of the exceedance of emission limits. Annual emissions are calculated monthly as the sum of each consecutive 12-month period. Compliance with these emission limits may be determined as stated in, but not limited to, Conditions 2, 3, 4, 5, 7, 8, 10, 11, 16, 18, 19, 25, 27, 28, 29, and 34.

(9 VAC 5-80-1470, 9 VAC 5-50-280, 9 VAC 5-50-410 and 40 CFR 63.43(g))

14. **Visible Emission Limit** – Visible emissions from the common exhaust stack with individual flues for the CFB boilers shall not exceed 10 percent opacity except during one six-minute period in any one hour in which visible emissions shall not exceed 20 percent opacity as determined by EPA Method 9 (reference 40 CFR 60, Appendix A). This condition applies at all times except during startup, shutdown, and malfunction.  
(9 VAC 5-80-1470, 9 VAC 5-50-80, 9 VAC 5-50-280 and 40 CFR 63.43(g))

15. **Requirements by Reference** – The permittee shall comply with all applicable requirements contained in 40 CFR Part 63, Subpart A.

- a. In particular, for the CFB boilers, the permittee shall comply with the following applicable requirements of 40 CFR 63, Subpart A, related to startup, shutdown, and malfunction, as defined at 40 CFR 63.2:
- i. The permittee shall at all times, including periods of startup, shutdown, and malfunction as defined at 40 CFR 63.2, operate the CFB boilers and associated air pollution control equipment and monitoring equipment, in a manner consistent with

- safety and good air pollution control practices for minimizing emissions to the levels required by the relevant standards, i.e., meet the emission standard(s) or comply with the applicable Startup, Shutdown, and Malfunction Plan (Plan), as required below. Determination of whether such operation and maintenance procedures are being used will be based on information available to the Department and USEPA, which may include, but is not limited to, monitoring results, review of operation and maintenance procedures (including the Plan), review of operation and maintenance records, and inspection of the CFB boilers.
- ii. The permittee shall correct malfunctions as soon as practicable after their occurrence in accordance with the applicable Plan. To the extent that an unexpected event arises during a startup, shutdown, or malfunction, the permittee shall comply by minimizing emissions during such a startup, shutdown, and malfunction event consistent with safety and good air pollution control practices.
  - iii. These operations and maintenance requirements, which are established pursuant to Section 112 of the Clean Air Act, are enforceable independent of applicable emissions limitations and other applicable requirements.
- b. The permittee shall develop, implement, and maintain written Startup, Shutdown, and Malfunction Plans (Plans) that describe, in detail, the plant during periods of startup, shutdown, and malfunction and a program of corrective action for a malfunctioning process, and air pollution control and monitoring equipment used to comply with the relevant emission standards. These Plans shall be developed to satisfy the purposes set forth in 40 CFR 63.6 (e) (3) (i) (A), (B) and (C). The permittee shall develop its initial Plans prior to the initial startup of an emissions unit(s).
- i. During periods of startup, shutdown, and malfunction of an emission unit, the permittee shall operate and maintain such unit, including associated air pollution control and monitoring equipment, in accordance with the procedures specified in the applicable Plan required in Condition 15.b.
  - ii. When actions taken by the permittee during a startup, shutdown, or malfunction (including actions taken to correct a malfunction) are consistent with the procedures specified in the applicable Plan, the permittee shall keep records for that event which demonstrate that the procedures specified in the Plan were followed. In addition, the permittee shall keep records of these events as specified in 40 CFR 63.10(b), including records of occurrence and duration of each startup, shutdown, or malfunction and monitoring equipment. Furthermore, the permittee shall confirm in the periodic compliance report that actions taken during periods of startup, shutdown, and malfunction were consistent with the applicable Plan, as required by 40 CFR 63.10 (d) (5).
  - iii. If an action taken by the permittee during a startup, shutdown, or malfunction (including an action taken to correct a malfunction) of an emission unit is not

consistent with procedures specified in the applicable Plan, and the emission unit exceeds a relevant emission standard, then the permittee must record the actions taken for that event and must promptly report such actions as specified by 40 CFR 63.6 (d) (5), unless otherwise specified elsewhere in this permit.

- iv. The permittee shall make changes to the Plan for an emission unit if required by the Department or USEPA, as provided for by 40 CFR 63.6 9 (e) (3) (vii), or as otherwise required by 40 CFR 63.6 (e) (viii).
- v. These Plans are records required by this permit, which the Permittee must retain in accordance with the general requirements for retention and availability of records. In addition, when the permittee revises a Plan, the permittee must also retain and make available the previous version of the Plan for a period of at least 5 years after such revision.

(9 VAC 5-80-1470 and 40 CFR Part 63, Subpart A)

#### **CONTINUOUS MONITORING SYSTEMS**

- 16. **Continuous Emission Monitoring Systems** – The permittee shall install, calibrate, maintain, operate and record the output of continuous emission monitoring systems (CEMS) for measuring emissions of carbon monoxide from each CFB boiler. Each CEMS shall be installed, calibrated, maintained, and operated in accordance with the applicable requirements of 40 CFR 60.13 and DEQ approved procedures.  
(9 VAC 5-80-1470, 9 VAC 5-50-40, 40 CFR 60.13 and 9 VAC 5-50-410)
- 17. **Continuous Emission Monitoring Systems** – The permittee shall install, calibrate, maintain, operate and record the output of continuous flow monitoring systems for measuring the volumetric flow rate of exhaust gases discharged to the atmosphere from each CFB boiler. Each flow monitoring system shall be installed, calibrated, maintained, and operated in accordance with the applicable requirements of 40 CFR 60.13, 40 CFR 60.49Da(l) or (m), and DEQ approved procedures.  
(9 VAC 5-80-1470, 9 VAC 5-50-40, 9 VAC 5-50-410 and 40 CFR 63.43(g))
- 18. **Continuous Emission Monitoring Systems** – The permittee shall install, calibrate, maintain, and operate a CEMS to measure and record the concentration of mercury in the exhaust gases from each CFB boiler, as follows:
  - a. The owner or operator must install, operate, and maintain each CEMS according to Performance Specification 12A in appendix B of 40 CFR Part 60.
  - b. The owner or operator must conduct a performance evaluation of each CEMS according to the requirements of 40 CFR 60.13 and Performance Specification 12A in appendix B of 40 CFR Part 60.

- c. The owner or operator must operate each CEMS in accordance with the following requirements:
  - i. As specified in 40 CFR 60.13(e)(2), each CEMS must complete a minimum of one cycle of operation (sampling, analyzing, and data recording) for each successive 15-minute period;
  - ii. The owner or operator must reduce CEMS data as specified in 40 CFR 60.13(h);
  - iii. The owner or operator shall use all valid data points collected during the hour to calculate the hourly average mercury concentration; and
  - iv. The owner or operator must record the results of each required certification and quality assurance test of the CEMS.
- d. Mercury CEMS data collection must conform to the following requirements:
  - i. For each calendar month in which the affected unit operates, valid hourly mercury concentration data, stack gas volumetric flow rate data, moisture data (if required), and electrical output data (i.e., valid data for all of these parameters) shall be obtained for at least 75 percent of the unit operating hours in the month.
  - ii. Data reported to meet the requirements of Condition 18.d.i. shall not include hours of unit startup, shutdown, or malfunction. In addition, data reported to meet the requirements of the Attachment to this permit shall not include data substituted using the missing data procedures in 40 CFR part 75, subpart D, nor shall the data have been bias adjusted according to the procedures of 40 CFR part 75.
  - iii. If valid data are obtained for less than 75 percent of the unit operating hours in a month, you must discard the data collected in that month and replace the data with the mean of the individual monthly emission rate values determined in the last 12 months. In the 12-month rolling average calculation, this substitute Hg emission rate shall be weighted according to the number of unit operating hours in the month for which the data capture requirement of Condition 18.d.i. was not met.
  - iv. Notwithstanding the requirements of Condition 15.a.iii., if valid data are obtained for less than 75 percent of the unit operating hours in another month in that same 12-month rolling average cycle, discard the data collected in that month and replace the data with the highest individual monthly emission rate determined in the last 12 months. In the 12-month rolling average calculation, this substitute mercury emission rate shall be weighted according to the number of unit operating hours in the month for which the data capture requirement of Condition 18.d.i. was not met.

The requirement to install, calibrate, maintain, and operate the mercury CEMS may be deferred upon written approval by DEQ in the event that the permittee makes an adequate demonstration that mercury CEMS are not reliable compliance indicators at the detection

levels needed to demonstrate compliance with this permit. For any period during which installation and operation of mercury CEMS is deferred, the permittee shall install, certify, maintain, and operate a sorbent trap monitoring system to measure the concentration of mercury in the exhaust gases from each CFB boiler, in accordance with the Attachment. (9 VAC 5-80-1470, 9 VAC 5-50-40, and 40 CFR 63.43(g))

19. **Continuous Monitoring Systems** – The permittee shall install, certify, maintain, operate and record the output of CEMS for measuring filterable PM emissions from each CFB boiler. Each CEMS shall be installed, certified, maintained and operated in accordance with the applicable requirements of 40 CFR 60.48Da(p) and 40 CFR 60.49Da(v), and DEQ approved procedures and shall reflect the level of technological advancement commensurate with the current state of technology in the industry.  
(9 VAC 5-80-1180 D, 9 VAC 5-80-1705 A, 40 CFR 60.48Da(o) and 9 VAC 5-50-410)

20. **Monitoring Plan** – The permittee shall prepare and submit for approval a unit-specific monitoring plan for each monitoring system for the CFB boilers, at least 45-days before commencing certification testing of the monitoring systems. The permittee shall comply with the requirements in the approved plan. The plan shall address the following:
- Installation of the CEMS sampling probe or other interface at a measurement location relative to each affected process unit such that the measurement is representative of the exhaust emissions;
  - Performance and equipment specifications for the sample interface, the pollutant concentration or parametric signal analyzer, and the data collection and reduction systems;
  - Performance evaluation procedures and acceptance criteria;
  - Ongoing operation and maintenance procedures, ongoing data quality assurance procedures and ongoing recordkeeping and reporting procedures in accordance with 40 CFR 60 Subpart Da, the general requirements of 40 CFR 60.13, 40 CFR part 75 and the Attachment as applicable.

(9 VAC 5-80-1470, 9 VAC 5-50-50, 40 CFR 60.49Da(s), 9 VAC 5-50-410 and 40 CFR 63.43(g))

21. **CEMS/COMS Performance Evaluations** – Performance evaluations of the continuous monitoring systems shall be conducted in accordance with 40 CFR Part 60, Appendix B, and shall take place during the performance tests under 9 VAC 5-50-30 or within 30 days thereafter. Two copies of the performance evaluations report shall be submitted to the Director, Southwest Regional Office within 60 days of the evaluation. The continuous monitoring systems shall be installed and operational prior to conducting initial performance tests. Verification of operational status shall, as a minimum, include completion of the manufacturer's written requirements or recommendations for installation, operation and

calibration of the device. A 30-day notification, prior to the demonstration of the continuous monitoring system's performance, and subsequent notifications shall be submitted to the Director, Southwest Regional Office.

(9 VAC 5-80-1470, 9 VAC 5-50-40, and 40 CFR 63.43(g))

22. **CEMS/COMS Quality Control Program** – A CEMS/COMS quality control program which meets the requirements of 40 CFR 60.13 and Appendix B or F as applicable shall be implemented for all continuous monitoring systems except that Relative Accuracy Test Audits (RATA's) may be required less frequently if approved by DEQ.

(9 VAC 5-80-1470, 9 VAC 5-50-40 and 40 CFR 63.43(g))

23. **Monitoring Devices** – The permittee shall install, calibrate, maintain, and operate the following:

- a. A meter measuring gross electrical output of the facility in megawatt hours (MWhr); and
- b. A meter measuring steam production for each CFB boiler.

Steam production measurements shall be used to allocate gross electrical output to each CFB boiler. Each meter shall be operated and the output recorded on a continuous basis. Each meter shall be provided with adequate access for inspection.

(9 VAC 5-80-1470, 40 CFR 60.49Da(k)(1), 9 VAC 5-50-410 and 40 CFR 63.43(g))

24. **Monitoring Devices** – The permittee shall install, calibrate, maintain, and operate a system for monitoring the throughput of each type of fuel to each CFB boiler. Each monitoring system shall be installed, calibrated and maintained in accordance with the manufacturer's recommendations at a minimum and shall be provided with adequate access for inspection.

(9 VAC 5-80-1470 and 40 CFR 63.43(g))

## **REPORTING**

25. **Excess Emissions Reports** – The permittee shall submit written reports to the Director, Southwest Regional Office of excess emissions from any process monitored by a continuous monitoring system (COMS/CEMS) on a quarterly basis, postmarked by the 30th day following the end of the calendar quarter. The permittee may submit the reports in electronic format as approved by DEQ. Each report shall include the following information, at a minimum:

- a. The magnitude of excess emissions, any conversion factors used in the calculation of excess emissions, and the date and time of commencement and completion of each period of excess emissions;
- b. Specific identification of each period of excess emissions that occurs during startups, shutdowns, and malfunctions of the process, the nature and cause of the malfunction (if known), the corrective action taken or preventative measures adopted;



- c. The date and time identifying each period during which the continuous monitoring system was inoperative except for zero and span checks and the nature of the system repairs or adjustments;
- d. When no excess emissions have occurred or the continuous monitoring systems have not been inoperative, repaired or adjusted, such information shall be stated in that report.

(9 VAC 5-80-1470, 9 VAC 5-50-50, 40 CFR 60.7, 40 CFR 60.51Da(i), 9 VAC 5-50-410 and 40 CFR 63.43(g))

26. **Semi-Annual Reports** – The permittee shall submit written reports to the Director, Southwest Regional Office for each continuous monitoring system on a semi-annual basis, postmarked by the 30th day following the end of each six-month period. The permittee may submit the reports in electronic format as approved by DEQ. Reports submitted in electronic format shall be submitted on a quarterly basis. Each report, written or electronic, shall include the following, at a minimum:

- a. Company name and address;
- b. Date of report and beginning and ending dates of the reporting period;
- c. A signed statement indicating whether:
  - i. The required continuous monitoring system calibration, span, and drift checks or other periodic audits have or have not been performed as specified;
  - ii. The data used to show compliance was or was not obtained in accordance with approved methods and procedures and is representative of plant performance;
  - iii. The minimum data requirements have or have not been met; or, the minimum data requirements have or have not been met for errors that were unavoidable. If the minimum quantity of emission data as required by 40 CFR 60.49Da is not obtained for any 30 successive boiler operating days, the information indicated in 40 CFR 60.51Da(c) shall be submitted; and
  - iv. Compliance with the standards has or has not been achieved during the reporting period.
- d. With regard to opacity monitoring for the CFB boilers:
  - i. Description of any modifications to the continuous opacity monitors, which could effect the ability of the COMS to comply with the performance specifications under 40 CFR 60, Appendix B; and

- ii. For any periods for which opacity data are not obtained, the permittee shall submit a signed statement indicating if any changes were made in operation of the emission control system during the period of data unavailability. Operations of the control system and the affected boiler during periods of data unavailability are to be compared with operation of the control system and the affected boiler before and following the period of data unavailability.
- e. With regard to mercury emissions and emissions monitoring for the CFB boilers:
  - i. The applicable mercury emission limit;
  - ii. The number of unit operating hours for each month in the reporting period;
  - iii. The number of unit operating hours with valid data for mercury concentration, stack gas flow rate, moisture (if required), and electrical output for each month in the reporting period;
  - iv. The monthly average ppmw mercury content of coal burned, the monthly average Btu value of coal burned, and the mercury emission rate in both lbs/month and lbs/MW-hr for each month in the reporting period;
  - v. The number of hours of valid data excluded from the calculation of the monthly mercury emission rate, due to unit startup, shutdown and malfunction for each month in the reporting period;
  - vi. The 12-month rolling average mercury emission rate in lbs/year for each month in the reporting period; and
  - vii. The data assessment report required by Appendix F to the Attachment.

One copy of the semi-annual report shall be submitted to the U.S. Environmental Protection Agency (USEPA) at the address specified in Condition 36.  
(9 VAC 5-80-1470, 9 VAC 5-170-160, 9 VAC 5-50-50, 9 VAC 5-50-410 and 40 CFR 63.43(g))

### **INITIAL COMPLIANCE DETERMINATION**

27. **Stack Test** – Initial performance tests shall be conducted for particulate matter, PM-10, carbon monoxide, volatile organic compounds, mercury, hydrogen chloride and hydrogen fluoride from each CFB boiler exhaust flue to determine compliance with the emission limits contained in Condition 13. Initial performance tests shall also be conducted for antimony, arsenic, beryllium, cadmium, chromium, cobalt, manganese, lead, nickel, and selenium compounds in order to verify that expected controlled emission rates provided in Virginia Electric and Power Company's application dated February 15, 2008 can be achieved. The test methods to be used are the following USEPA reference methods, except that equivalent

test methods may be substituted upon request, if approved by the Director, Southwest Regional Office, as equivalent and allowable by applicable regulations:

<u>Pollutant</u>	<u>Test Method</u>
Filterable Particulate Matter	EPA Method 5
Total PM-10	EPA Method 201A and 202
Condensable PM-10	EPA Method 202
Antimony Compounds	EPA Method 29
Beryllium Compounds	EPA Method 29
Cadmium Compounds	EPA Method 29
Manganese Compounds	EPA Method 29
Lead Compounds	EPA Method 29
Nickel Compounds	EPA Method 29
Selenium Compounds	EPA Method 29
Carbon Monoxide	EPA Method 10
Volatile Organic Compounds	EPA Methods 25A
Mercury	EPA Method 101A
Hydrogen Chloride	EPA Method 26A
Hydrogen Fluoride	EPA Method 26A

The tests shall be performed and reported within 60 days after achieving the maximum production rate at which the facility will be operated but in no event later than 180 days after start-up of the permitted facility. Tests shall be conducted and reported and data reduced as set forth in 9 VAC 5-50-30 and 9 VAC 5-60-30, and the test methods and procedures contained in each applicable section or subpart listed in 9 VAC 5-50-410. The details of the tests are to be arranged with the Director, Southwest Regional Office. The permittee shall submit a test protocol at least 30 days prior to testing. Two copies of the test results shall be submitted to the Director, Southwest Regional Office within 45 days after test completion and shall conform to the test report format enclosed with this permit.

The permittee shall perform an initial stack test for PM-2.5 in the time frames as required for testing the other pollutants in this condition if a test method for PM-2.5 has received final approval by the USEPA or DEQ at that time. If a test method for PM-2.5 has not received final approval by the USEPA or DEQ at the time initial testing as required in this condition is to be conducted, the permittee shall perform initial stack testing for PM-2.5 within 60 days of final approval of a test method by USEPA or DEQ, or as required by the Director, Southwest Regional Office.

(9 VAC 5-80-1490, 9 VAC 5-50-30, 9 VAC 5-50-410 and 40 CFR 63.43(g))

28. **Visible Emissions Evaluation** – Concurrently with the initial performance tests, visible emission evaluations (VEE) in accordance with 40 CFR Part 60, Appendix A, Method 9, shall also be conducted by the permittee on the common exhaust stack for the CFB boilers and auxiliary boiler. Each test shall consist of 30 sets of 24 consecutive observations (at 15 second intervals) to yield a six minute average. The details of the tests are to be arranged with the Director, Southwest Regional Office. The permittee shall submit a test protocol at least 30 days prior to testing. The evaluation shall be performed and reported within 60 days after achieving the maximum production rate at which the facility will be operated but in no event later than 180 days after start-up of the permitted facility. Should conditions prevent concurrent opacity observations, the Director, Southwest Regional Office shall be notified in writing, within seven days, and visible emissions testing shall be rescheduled within 30 days. Rescheduled testing shall be conducted under the same conditions (as possible) as the initial performance tests. Two copies of the test result shall be submitted to the Director, Southwest Regional Office within 45 days after test completion and shall conform to the test report format enclosed with this permit.

(9 VAC 5-80-1490, 9 VAC 5-50-30, 40 CFR 60.50Da(b)(3), 9 VAC 5-50-410 and 40 CFR 63.43(g))

### **CONTINUING COMPLIANCE DETERMINATION**

29. **Stack Tests** – Annually and upon request by the DEQ, the permittee shall conduct performance tests for carbon monoxide, particulate matter, PM-10, volatile organic compounds, mercury, hydrogen chloride and hydrogen fluoride from each CFB boiler exhaust to demonstrate compliance with the emission limits contained in this permit. In a calendar year when a relative accuracy test audit (RATA) is conducted on a CEMS, then a stack test for the pollutant monitored by that CEMS is not required. The permittee shall conduct annual performance tests for PM-2.5 emissions from each CFB boiler upon USEPA or DEQ final approval of a test method, or as required by the Director, Southwest Regional Office. The details of the tests shall be arranged with the Director, Southwest Regional Office. In addition to performance tests, continuous compliance with emission standards and permit limits shall be determined by CEMS data.

(9 VAC 5-80-1490, 9 VAC 5-50-30 G and 40 CFR 63.43(g))

30. **Stack Tests** – If results of the initial performance test indicate PM-10 emissions from the CFB boilers exceed the PM-10 emission limit in lb/MMBtu in this permit, the permittee shall

complete an optimization of all equipment affecting such emissions and retest for PM-10 emissions from the CFB boilers in accordance with the following:

- a. The permittee shall submit to the Director, Southwest Regional Office for approval a plan for optimizing the performance of all equipment affecting PM-10 emissions. The optimization plan shall be submitted within 60 days of reporting to DEQ the results of the initial performance test.
- b. The permittee shall complete the approved optimization and notify the Director, Southwest Regional Office in writing of such completion within 180 days of DEQ approval of the optimization plan. If additional time is needed to complete the optimization plan, the permittee may submit a written request for additional time to the Director, Southwest Regional Office.
- c. The permittee shall conduct and report the results of a performance test for PM-10 emissions from the CFB boilers within 60 days of completion of the optimization plan. The details of the test shall be arranged with the Director, Southwest Regional Office.

If results of the retest required in paragraph c. of this condition indicate an exceedance of the PM-10 emission limit and the permittee can demonstrate to the satisfaction of the DEQ that the actual condensable portion of PM-10 causes the exceedance, a change to the permit in accordance with 9 VAC 5-80-1925, shall be initiated within 30 days of reporting to DEQ the results of the retest to revise the PM-10 emission limit to the optimized rate up to a maximum of 0.030 lb/MMBtu. During implementation of the optimization plan, retest or permit change as required in this condition, failure to meet the PM-10 emission limits in this permit for the CFB boilers shall not be considered a violation by DEQ provided the filterable PM-10 emissions, as determined by EPA Method 201A, do not exceed 0.010 lb/MMBtu and the total PM-10 emissions, including the condensable PM-10 emissions, as determined by EPA Methods 201A and 202, or other methods as approved by DEQ, do not exceed 0.030 lb/MMBtu.

(9 VAC 5-80-1490, 9 VAC 5-50-30 G and 40 CFR 63.43(g))

31. **Stack Tests** – If results of the initial stack test indicate hydrogen fluoride emissions from the CFB boilers exceed the hydrogen fluoride emission limits in this permit, the permittee shall complete an optimization of all equipment affecting such emissions and retest for hydrogen fluoride emissions from the CFB boilers in accordance with the following:
  - a. The permittee shall submit to the Director, Southwest Regional Office for approval a plan for optimizing the performance of all equipment affecting hydrogen fluoride emissions. The optimization plan shall be submitted within 60 days of reporting to DEQ the results of the initial performance test.
  - b. The permittee shall complete the approved optimization and notify the Director, Southwest Regional Office in writing of such completion within 180 days of DEQ approval of the optimization plan. If additional time is needed to complete the

optimization plan, the permittee may submit a written request for additional time to the Director, Southwest Regional Office.

- c. The permittee shall conduct and report the results of a performance test for hydrogen fluoride emissions from the CFB boilers within 60 days of completion of the optimization plan. The details of the test shall be arranged with the Director, Southwest Regional Office. The performance test shall include a fuel analysis and stack tests performed simultaneously on the inlet and outlet of each CFB boiler fabric filter baghouse to determine the hydrogen fluoride emission reduction.

If results of the retest required in paragraph c. of this condition indicate an exceedance of the hydrogen fluoride emission limit, a change to the permit in accordance with 9 VAC 5-80-1925, shall be initiated within 30 days of reporting to DEQ the results of the retest to revise the hydrogen fluoride emission limit to the optimized rate up to a maximum rate of 0.0023 lb/MMBtu. During implementation of the optimization plan, retest or permit change as required in this condition, failure to meet the hydrogen fluoride emission limit in this permit shall not be considered a violation by DEQ so long as hydrogen fluoride emissions do not exceed 0.0023 lb/MMBtu.

(9 VAC 5-80-1490, 9 VAC 5-50-30 G and 40 CFR 63.43(g))

32. **Stack Tests** – If results of the initial stack test indicate mercury emissions from the CFB boilers exceed the mercury emission limit in this permit, the permittee shall complete an optimization of all equipment affecting such emissions and retest for mercury emissions from the CFB boilers in accordance with the following:

- a. The permittee shall submit to the Director, Southwest Regional Office for approval a plan for optimizing the performance of all equipment affecting mercury emissions. The optimization plan shall be submitted within 60 days of reporting to DEQ the results of the initial performance test.
- b. The permittee shall complete the approved optimization and notify the Director, Southwest Regional Office in writing of such completion within 180 days of DEQ approval of the optimization plan. If additional time is needed to complete the optimization plan, the permittee may submit a written request for additional time to the Director, Southwest Regional Office.
- c. The permittee shall conduct and report the results of a performance test for mercury emissions from the CFB boilers within 60 days of completion of the optimization plan. The details of the test shall be arranged with the Director, Southwest Regional Office. The performance test shall include a fuel analysis and stack tests performed simultaneously on the inlet and outlet of each CFB boiler fabric filter baghouse to determine the mercury emission reduction.

(9 VAC 5-80-1490, 9 VAC 5-50-30 G and 40 CFR 63.43(g))

33. **Stack Tests** – There is limited experience with electric generating units operating under MACT limits for mercury. Therefore, if the permittee reasonably demonstrates using operational and other related information collected for a period not shorter than the first 12 months of operation of all the equipment used to control mercury (including limestone injection, fluidized gas desulfurization, activated carbon injection, fabric filters and good combustion practices) that the lb/MWhr limit is not achievable on a consistent basis under reasonably foreseeable conditions, then testing and evaluation shall be conducted to determine an appropriate adjusted maximum achievable annual emission limit in accordance with the following procedure:
- a. In order to obtain an adjustment of the lb/MWhr MACT limit for mercury set forth in this permit, the permittee shall submit to the Director, Southwest Regional Office for approval a protocol for the testing of mercury 30 days prior to testing. In addition, the permittee shall submit to the Director, Southwest Regional Office for approval an analysis of the mercury content of the fuel combusted by the facility during the history of its operation. The permittee shall submit to the Director, Southwest Regional Office the test results and any calculations and assumptions used to develop an adjusted MACT annual permit limit for mercury within 45 days of testing.
  - b. The permit may be amended to incorporate an adjusted lb/MWhr MACT mercury limit in accordance with Article 7 of the State Air Pollution Control Board Regulations. The adjusted MACT limit shall be based on operational and other related information available no less than 12 months after the commencement of operations using all available control equipment.
  - c. During any period after the first 12 months of operation in which the permittee has applied for an adjusted lb/MWhr MACT limit for mercury but before one becomes effective or such application is denied by the Department, the plant shall be deemed to be in compliance with its mercury emissions as long as the plant is using the equipment installed at the plant and good air pollution control practices to minimize mercury emissions to the maximum extent achievable. At that time, the permittee shall demonstrate compliance by the use of such equipment and practices based on a protocol to be submitted for approval prior to commencement of operations and amended to account for actual operations. The protocol shall include the optimization of activated carbon injection.
- (9 VAC 5-80-1490, 9 VAC 5-50-30 G and 40 CFR 63.43(g))
34. **Carbon Monoxide Emissions Compliance Determination** – The average carbon monoxide emission rate for each CFB boiler shall be used to demonstrate compliance with the emission limit of 0.15 lb/MMBtu applicable at loads equal to or greater than 75 percent of maximum. The permittee shall calculate the average carbon monoxide emission rate for each CFB boiler using all valid CEMS values measured at loads of 75 percent or greater for each rolling 30-day period using the following formula:

$$ER_{CO\ 30d\ H} = \frac{\sum_{i=1}^n ER_i}{n}$$

where,

$ER_{CO\ 30d\ H}$  = 30-day average carbon monoxide emission rate, for the load range of 75 percent and greater; lb/MMBtu  
 $ER_i$  = the incremental CEMS-measured carbon monoxide emission rate at loads of 75 percent and greater; lb/MMBtu  
 $i$  = incremental CEMS reading  
 $n$  = the number of incremental CEMS readings in the rolling 30-day period when the heat input rate was in the load range of 75 percent and greater

The 30-day load weighted average carbon monoxide emission rate for each CFB boiler shall be used to demonstrate compliance with the emission limit calculated in accordance with Condition 13, for loads less than 75 percent of maximum. The permittee shall calculate the 30-day load weighted average carbon monoxide emission rate for each CFB boiler using all valid CEMS values measured at all loads greater than zero using the following formula:

$$ER_{CO\ 30d\ L} = \frac{\sum_{i=1}^n ER_i \times IR_i}{\sum_{i=1}^n IR_i}$$

where,

$ER_{CO\ 30d\ L}$  = 30-day weighted average carbon monoxide emission rate; lb/MMBtu  
 $ER_i$  = the incremental hour's CEMS-measured carbon monoxide emission rate; lb/MMBtu  
 $IR_i$  = the heat input rate corresponding to the incremental CEMS reading; MMBtu  
 $i$  = incremental CEMS reading having a non-zero heat input rate  
 $n$  = the number of incremental CEMS readings in the rolling 30-day period when there is a heat input rate

Maximum load for each CFB boiler is considered to be 3,132 MMBtu/hr heat input. The requirements of this condition shall not limit the validity or use of other methods of compliance determination as may be required in this permit or approved by DEQ.  
 (9 VAC 5-80-1470, 9 VAC 5-170-160 and 40 CFR 63.43(g))



## **RECORDS**

35. **On Site Records** – The permittee shall maintain records of emission data and operating parameters as necessary to demonstrate compliance with this permit. The content and format of such records shall be arranged with the Director, Southwest Regional Office. These records shall include, but are not limited to:

- a. Monthly and annual heat input to each CFB boiler. Annual heat input shall be calculated monthly as the sum of each consecutive 12-month period. Compliance for the consecutive 12-month period shall be demonstrated monthly by adding the total for the most recently completed calendar month to the individual monthly totals for the preceding 11 months.
- b. Monthly and annual throughput of each type of fuel and limestone to each CFB boiler. Annual throughput shall be calculated monthly as the sum of each consecutive 12-month period. Compliance for the consecutive 12-month period shall be demonstrated monthly by adding the total for the most recently completed calendar month to the individual monthly totals for the preceding 11 months.
- c. Monthly and annual amounts of each type of fuel delivered to the facility. Annual amounts shall be calculated monthly as the sum of each consecutive 12-month period. Compliance for the consecutive 12-month period shall be demonstrated monthly by adding the total for the most recently completed calendar month to the individual monthly totals for the preceding 11 months.
- d. Emissions calculations, based on data from fuel analyses, stack tests and CEMS, for each CFB boiler using calculation methods approved by the Director, Southwest Regional Office, to verify compliance with the applicable emission limits in this permit.
- e. Carbon monoxide emission limit calculations in accordance with Condition 13.
- f. Carbon monoxide emission rate calculations in accordance with Condition 34.
- g. All fuel supplier certifications.
- h. Results of each as-fired fuel sample analysis.
- i. Annual sulfur content of coal and coal refuse determined on a 12-month rolling average basis using results from weekly sampling and analysis required in Condition 9.
- j. Information required in each Excess Emission Report and continuous monitoring system Semi-Annual Report as required in this permit.
- k. Gross electrical output, in MWhr, for the facility and steam production for each CFB.
- l. Scheduled and unscheduled maintenance and operator training.

- m. Continuous monitoring system calibrations and calibration checks, percent operating time, excess emissions, and adjustments and maintenance performed on continuous monitoring systems and devices.
- n. Results of all stack tests, visible emission evaluations and performance evaluations.

These records shall be available for inspection by the DEQ and shall be current for the most recent five years.

(9 VAC 5-80-1470, 9 VAC 5-50-50, 9 VAC 5-50-410 and 40 CFR 63.43(g))

### **NOTIFICATIONS**

36. **Initial Notifications** – The permittee shall furnish written notification to the Director, Southwest Regional Office of:

- a. The actual date on which construction of the CFB boilers commenced within 30 days after such date.
- b. The actual start-up date of the CFB boilers within 15 days after such date.
- c. The anticipated date of continuous monitoring system performance evaluations postmarked not less than 30 days prior to such date.
- d. The anticipated date of performance tests of the CFB boilers postmarked at least 30 days prior to such date.

Copies of the written notifications referenced in this condition are to be sent to:

Associate Director  
Office of Air Enforcement (3AP10)  
U.S. Environmental Protection Agency  
Region III  
1650 Arch Street  
Philadelphia, PA 19103-2029

(9 VAC 5-80-1470, 9 VAC 5-50-50 and 40 CFR 63.43(g))

### **GENERAL CONDITIONS**

37. **Permit Invalidation** – This permit to construct the CFB boilers shall become invalid, unless an extension is granted by the DEQ, if:

- a. A program of continuous construction is not commenced within 18 months from the date of this permit; or

- b. A program of construction is discontinued for a period of 18 months or more, or is not completed within a reasonable time, except for a DEQ approved period between phases of a phased construction project.

(9 VAC 5-80-1500)

38. **Changes to Permits** – Changing, amending, and reopening this permit may be initiated by the DEQ or the permittee and shall be made as specified in 9 VAC 5-80-1540.  
(9 VAC 5-80-1540)

39. **Permit Suspension/Revocation** – This permit may be suspended or revoked if the permittee:

- a. Knowingly makes material misstatements in the permit application or any amendments to it;
- b. Fails to comply with the terms or conditions of this permit;
- c. Fails to comply with any emission standards applicable to a permitted emissions unit; or
- d. Fails to comply with the applicable provisions of Article 7.

(9 VAC 5-80-1500 F)

40. **Right of Entry** – The permittee shall allow authorized local, state, and federal representatives, upon the presentation of credentials:

- a. To enter upon the permittee's premises on which the facility is located or in which any records are required to be kept under the terms and conditions of this permit;
- b. To have access to and copy at reasonable times any records required to be kept under the terms and conditions of this permit or the State Air Pollution Control Board Regulations;
- c. To inspect at reasonable times any facility, equipment, or process subject to the terms and conditions of this permit or the State Air Pollution Control Board Regulations; and
- d. To sample or test at reasonable times.

For purposes of this condition, the time for inspection shall be deemed reasonable during regular business hours or whenever the facility is in operation. Nothing contained herein shall make an inspection time unreasonable during an emergency.

(9 VAC 5-80-1470 and 9 VAC 5-170-130)

41. **Maintenance/Operating Procedures** – The permittee shall take the following measures in order to minimize the duration and frequency of excess emissions, with respect to air pollution control equipment and process equipment which affect such emissions:

- a. Develop a maintenance schedule and maintain records of all scheduled and non-scheduled maintenance.
- b. Maintain an inventory of spare parts.
- c. Have available written operating procedures for equipment. These procedures shall be based on the manufacturer's recommendations, at a minimum.
- d. Train operators in the proper operation of all such equipment and familiarize the operators with the written operating procedures, prior to their first operation of such equipment. The permittee shall maintain records of the training provided including the names of trainees, the date of training and the nature of the training

Records of maintenance and training shall be maintained on site for a period of five years and shall be made available to DEQ personnel upon request.

(9 VAC 5-80-1470 and 9 VAC 5-50-20 E)

42. **Record of Malfunctions** – The permittee shall maintain records of the occurrence and duration of any bypass, malfunction, shutdown or failure of the facility or its associated air pollution control equipment that results in excess emissions for more than one hour. Records shall include the date, time, duration, description (emission unit, pollutant affected, cause), corrective action, preventive measures taken and name of person generating the record.  
(9 VAC 5-80-1470 and 9VAC 5-20-180 J)

43. **Notification for Facility or Control Equipment Malfunction** – The permittee shall furnish notification to the Director, Southwest Regional Office of malfunctions of the affected facility or related air pollution control equipment that may cause excess emissions for more than one hour, by facsimile transmission, telephone or telegraph. Such notification shall be made as soon as practicable but no later than four daytime business hours after the malfunction is discovered. The permittee shall provide a written statement giving all pertinent facts, including the estimated duration of the breakdown, within two weeks of discovery of the malfunction. When the condition causing the failure or malfunction has been corrected and the equipment is again in operation, the permittee shall notify the Director, Southwest Regional Office.  
(9 VAC 5-80-1470 and 9 VAC 5-20-180 C)

44. **Notification for Control Equipment Maintenance** – The permittee shall furnish notification to the Director, Southwest Regional Office of the intention to shut down or bypass, or both, air pollution control equipment for necessary scheduled maintenance, which results in excess emissions for more than one hour, at least 24 hours prior to the shutdown. The notification shall include, but is not limited to, the following information:

- a. Identification of the air pollution control equipment to be taken out of service, as well as its location, and registration number;

- b. The expected length of time that the air pollution control equipment will be out of service;
- c. The nature and quantity of emissions of air pollutants likely to occur during the shutdown period;
- d. Measures that will be taken to minimize the length of the shutdown or to negate the effect of the outage.

(9 VAC 5-80-1470 and 9 VAC 5-20-180 B)

- 45. **Violation of Ambient Air Quality Standard** – The permittee shall, upon request of the DEQ, reduce the level of operation or shut down a facility, as necessary to avoid violating any primary ambient air quality standard and shall not return to normal operation until such time as the ambient air quality standard will not be violated.  
(9 VAC 5-80-1470 and 9 VAC 5-20-180 I)
- 46. **Transfer of Permits** – No person shall transfer this permit from one location to another or from one piece of equipment to another, except for the relocation of portable facilities that are exempt from the provisions of 9 VAC 5-80-1605, et seq., by 9 VAC 5-80-1695 A.2.  
(9 VAC 5-80-1530 A and C)
- 47. **Change of Ownership** – In the case of a transfer of ownership of a stationary source, the new owner shall abide by any current permit issued to the previous owner. The new owner shall notify the Director, Southwest Regional Office of the change of ownership within 30 days of the transfer.  
(9 VAC 5-80-1530 B)
- 48. **Existence of Permit No Defense** – The existence of this permit shall not constitute a defense to a violation of the Virginia Air Pollution Control Law (§10.1-1300 et seq. of the Code of Virginia) or the regulations of the board and shall not relieve any owner of the responsibility to comply with any applicable regulations, laws, ordinances and orders of the governmental entities having jurisdiction.  
(9 VAC 5-80-1510)
- 49. **Registration/Update** – Annual requirements to fulfill legal obligations to maintain current stationary source emissions data will necessitate a prompt response by the permittee to requests by the DEQ or the Board for information to include, as appropriate: process and production data; changes in control equipment; and operating schedules. Such requests for information from the DEQ will either be in writing or by personal contact. The availability of information submitted to the DEQ or the Board will be governed by applicable provisions of the Freedom of Information Act, §§ 2.1-340 through 2.1-348 of the Code of Virginia, § 10.1-1314 (addressing information provided to the Board) of the Code of Virginia, and 9 VAC 5-170-60 of the State Air Pollution Control Board Regulations. Information provided

to federal officials is subject to appropriate federal law and regulations governing confidentiality of such information.

(9 VAC 5-80-1470, 9 VAC 5-170-60 and 9 VAC 5-20-160)

50. **Permit Copy** – The permittee shall keep a copy of this permit on the premises of the facility to which it applies.

(9 VAC 5-80-1470)

## **SOURCE TESTING REPORT FORMAT**

### Report Cover

1. Plant name and location
2. Units tested at source (indicate Ref. No. used by source in permit or registration)
3. Test Dates.
4. Tester; name, address and report date

### Certification

1. Signed by team leader/certified observer (include certification date)
2. Signed by responsible company official
3. \*Signed by reviewer

### Copy of approved test protocol

### Summary

1. Reason for testing
2. Test dates
3. Identification of unit tested & the maximum rated capacity
4. \*For each emission unit, a table showing:
  - a. Operating rate
  - b. Test Methods
  - c. Pollutants tested
  - d. Test results for each run and the run average
  - e. Pollutant standard or limit
5. Summarized process and control equipment data for each run and the average, as required by the test protocol
6. A statement that test was conducted in accordance with the test protocol or identification & discussion of deviations, including the likely impact on results
7. Any other important information

### Source Operation

1. Description of process and control devices
2. Process and control equipment flow diagram
3. Sampling port location and dimensioned cross section Attached protocol includes: sketch of stack (elevation view) showing sampling port locations, upstream and downstream flow disturbances and their distances from ports; and a sketch of stack (plan view) showing sampling ports, ducts entering the stack and stack diameter or dimensions

### Test Results

1. Detailed test results for each run
2. \*Sample calculations
3. \*Description of collected samples, to include audits when applicable

### Appendix

1. \*Raw production data
2. \*Raw field data
3. \*Laboratory reports
4. \*Chain of custody records for lab samples
5. \*Calibration procedures and results
6. Project participants and titles
7. Observers' names (industry and agency)
8. Related correspondence
9. Standard procedures

\* Not applicable to visible emission evaluations

## **Attachment: Mercury Monitoring Provisions**

### **75.80 General provisions.**

(a) While operating each CFB boiler, the permittee shall not discharge, or allow to be discharged emissions of Hg to the atmosphere without accounting for all such emissions in accordance with the applicable provisions of this attachment.

(b) The permittee shall not disrupt the mercury continuous emission monitoring system, any portion thereof, or any other approved emission monitoring method, and thereby avoid monitoring and recording Hg mass emissions discharged into the atmosphere, except for periods of recertification or periods when calibration, quality assurance testing, or maintenance is performed in accordance with the provisions applicable to monitoring systems under 75.81 of this attachment.

(c) The permittee shall not retire or permanently discontinue use of the mercury continuous emission monitoring system, any component thereof, or any other approved emission monitoring system under this part, except under any one of the following circumstances:

(i) The permittee is monitoring Hg mass emissions from the CFB boilers with another certified monitoring system approved, in accordance with the provisions of paragraph (d) of this section; or

(ii) The responsible official submits notification of the date of certification testing of a replacement monitoring system in accordance with 40 CFR 75.61.

(d) The permittee shall comply with the applicable initial certification and recertification procedures in 40 CFR 75.20 and 40 CFR 75.70(d).

(e) For units that use continuous emission monitoring systems to account for Hg mass emissions, the permittee shall meet the applicable quality assurance and quality control requirements in 40 CFR 75.21 and appendix B to this attachment for the flow monitoring systems, Hg concentration monitoring systems, moisture monitoring systems, and diluent monitors required under 40 CFR 75.81. Units using sorbent trap monitoring systems shall meet the applicable quality assurance requirements in 40 CFR 75.15, appendix K to this attachment, and sections 1.5 and 2.3 of appendix B to this attachment.

(f) Except as provided in 40 CFR 75.38(b), the permittee shall provide substitute data from monitoring systems required under 75.81 of this attachment for each CFB boiler as follows:

(1) When using an Hg concentration monitoring system, the permittee shall substitute for missing data in accordance with the applicable missing data procedures in 40 CFR 75.31 through 75.38 whenever the CFB boiler combusts fuel and:



## **Attachment: Mercury Monitoring Provisions**

- (i) A valid, quality-assured hour of Hg concentration data (in  $\mu\text{gm}/\text{scm}$ ) has not been measured and recorded, either by a certified Hg concentration monitoring system, by an appropriate EPA reference method under 40 CFR 75.22, or by an approved alternative monitoring method under 40 CFR 75 subpart E; or
  - (ii) A valid, quality-assured hour of flow rate data (in scfh) has not been measured and recorded for a unit either by a certified flow monitor, by an appropriate EPA reference method under 40 CFR 75.22, or by an approved alternative monitoring system under 40 CFR 75 subpart E; or
  - (iii) A valid, quality-assured hour of moisture data (in percent  $\text{H}_2\text{O}$ ) has not been measured or recorded for an affected unit, either by a certified moisture monitoring system, by an appropriate EPA reference method under 40 CFR 75.22, or an approved alternative monitoring method under 40 CFR 75 subpart E. This requirement does not apply when a default percent moisture value, as provided in 40 CFR 75.11(b), is used to account for the hourly moisture content of the stack gas, or when correction of the Hg concentration for moisture is not necessary; or
  - (iv) A valid, quality-assured hour of heat input rate data (in  $\text{MMBtu}/\text{hr}$ ) has not been measured and recorded for a unit, either by certified flow rate and diluent ( $\text{CO}_2$  or  $\text{O}_2$ ) monitors, by appropriate EPA reference methods under 40 CFR 75.22, or by approved alternative monitoring systems under 40 CFR 75 subpart E.
- (2) When using a sorbent trap monitoring system to quantify Hg mass emissions, the permittee shall substitute for missing data in accordance with the missing data procedures in 40 CFR 75.39.

### **75.81 Monitoring of Hg mass emissions and heat input at the unit level.**

For each CFB boiler, the permittee shall either meet the general operating requirements in 40 CFR 75.10 for the following continuous emission monitors:

- (1) A Hg concentration monitoring system (as defined in 40 CFR 72.2) or a sorbent trap monitoring system (as defined in 40 CFR 72.2), to measure the mass concentration of total vapor phase Hg in the flue gas, including the elemental and oxidized forms of Hg, in micrograms per standard cubic meter ( $\mu\text{g}/\text{scm}$ ); and
- (2) A flow monitoring system; and
- (3) A continuous moisture monitoring system (if correction of Hg concentration for moisture is required), as described in 40 CFR 75.11(b). Alternatively, the permittee may use the appropriate fuel-specific default moisture value provided in 40 CFR 75.11, or a site-specific moisture value approved by petition under 40 CFR 75.66; and
- (4) The permittee must meet the general operating requirements for a flow monitoring system and an  $\text{O}_2$  or  $\text{CO}_2$  monitoring system to measure heat input rate.

## **Attachment: Mercury Monitoring Provisions**

### **75.82 Calculation of Hg mass emissions and heat input rate.**

The permittee shall calculate Hg mass emissions and heat input rate in accordance with the procedures in sections 9.1 through 9.3 of appendix F to this attachment.

### **75.83 Recordkeeping and reporting.**

(a) *General recordkeeping provisions.* The permittee shall maintain for each CFB boiler a file of all measurements, data, reports, and other information required by this attachment at the source in a form suitable for inspection for at least 3 years from the date of each record. Except for the certification data required in 40 CFR 75.57(a)(4) and the initial submission of the monitoring plan required in 40 CFR 75.57(a)(5), the data shall be collected beginning with the date of provisional certification. The certification data required in 40 CFR 75.57(a)(4) shall be collected beginning with the date of the first certification test performed. The file shall contain the following information:

(1) The information required in 40 CFR 75.57(a)(2), (a)(4), (a)(5), (a)(6), (b), (c)(2), (g) (if applicable), (h), and (i) or (j) (as applicable). For the information in 40 CFR 75.57(a)(2);

(2) The information required in 40 CFR 75.58(b)(3);

(3) For affected units using Hg CEMS or sorbent trap monitoring systems, for each hour when the unit is operating, record the Hg mass emissions, calculated in accordance with section 9 of appendix F to this attachment.

(4) Heat input and Hg methodologies for the hour; and

(5) Formulas from monitoring plan for total Hg mass emissions and heat input rate;

(b) *Certification, quality assurance and quality control record provisions.* The permittee shall record the applicable information in 40 CFR 75.59 for each CFB boiler.

(c) *Monitoring plan recordkeeping provision.* (1) *General provisions.* The permittee shall prepare and maintain a monitoring plan for each CFB boiler. The monitoring plan shall contain sufficient information on the continuous monitoring systems and the use of data derived from these systems to demonstrate that all the unit's Hg emissions are monitored and reported.

(2) *Updates.* Whenever the permittee makes a replacement, modification, or change in a certified continuous monitoring system or alternative monitoring system under 40 CFR 75 subpart E, including a change in the automated data acquisition and handling system or in the flue gas handling system, that affects information reported in the monitoring plan (e.g., a change to a serial number for a component of a monitoring system), then the permittee shall update the monitoring plan.

## **Attachment: Mercury Monitoring Provisions**

(3) *Contents of the monitoring plan.* Each monitoring plan shall contain the information in 40 CFR 75.53(g)(1) in electronic format and the information in 40 CFR 75.53(g)(2) in hardcopy format.

(d) *General reporting provisions.* (1) The responsible official shall comply with all reporting requirements in this attachment.

(2) The responsible official shall submit the following for each CFB boiler:

(i) Initial certification and recertification applications in accordance with 40 CFR 75.80(d);

(ii) Monitoring plans in accordance with paragraph (e) of this section; and

(iii) Quarterly reports in accordance with paragraph (f) of this section.

(3) *Quality assurance RATA reports.* The responsible official shall submit the quality assurance RATA report for each CFB boiler no later than 45 days after completing a quality assurance RATA according to section 2.3 of appendix B to this attachment. The responsible official shall report the hardcopy information required by 40 CFR 75.59(a)(9) to the Director, Southwest Regional Office.

(4) *Notifications.* The responsible official shall submit written notice to the Director, Southwest Regional Office according to the provisions in 40 CFR 75.61 for each CFB boiler.

(e) *Monitoring plan reporting* —(1) *Electronic submission.* The responsible official shall submit to the DEQ a complete, electronic, up-to-date monitoring plan file for each CFB boiler, as follows: No later than 21 days prior to the commencement of initial certification testing; at the time of a certification or recertification application submission; and whenever an update of the electronic monitoring plan is required, either under 40 CFR 75.53 or elsewhere in this attachment.

(2) *Hardcopy submission.* The responsible official shall submit all of the hardcopy information required under 40 CFR 75.53, for each CFB boiler, to the permitting authority prior to initial certification. Thereafter, the responsible official shall submit hardcopy information only if that portion of the monitoring plan is revised. The responsible official shall submit the required hardcopy information as follows: no later than 21 days prior to the commencement of initial certification testing; with any certification or recertification application, if a hardcopy monitoring plan change is associated with the recertification event; and within 30 days of any other event with which a hardcopy monitoring plan change is associated, pursuant to 40 CFR 75.53(b). Electronic submittal of all monitoring plan information, including hardcopy portions, is permissible provided that a paper copy of the hardcopy portions can be furnished upon request.

## **Attachment: Mercury Monitoring Provisions**

(f) *Quarterly reports* —(1) *Submission*. Quarterly reports shall be submitted, beginning with the calendar quarter containing the provisional certification. The responsible official shall report the data and information in this paragraph (f)(1) and the applicable compliance certification information in paragraph (f)(2) of this section to the Director, Southwest Regional Office quarterly. Each report must be submitted to the Director, Southwest Regional Office within 30 days following the end of each calendar quarter. Except as otherwise provided in 40 CFR 75.64(a)(4) and (a)(5), each report shall include the date of report generation and the following information for each CFB boiler:

(i) The facility information in 40 CFR 75.64(a)(3); and

(ii) The information and hourly data required in paragraphs (a) and (b) of this section, except for:

(A) Descriptions of adjustments, corrective action, and maintenance;

(B) Additional information including but not limited to field data sheets, lab analyses, quality control plan;

(C) The parametric information in 40 CFR 75.58(b)(3);

(D) Information required by 40 CFR 75.57(h) concerning the causes of any missing data periods and the actions taken to cure such causes;

(E) Hardcopy monitoring plan information required by 40 CFR 75.53 and hardcopy test data and results required by 40 CFR 75.59;

(F) Records of flow polynomial equations and numerical values required by 40 CFR 75.59(a)(5)(vi);

(G) Stratification test results required as part of the RATA supplementary records under 40 CFR 75.59(a)(7);

(H) Data and results of RATAs that are aborted or invalidated due to problems with the reference method or operational problems with the unit and data and results of linearity checks that are aborted or invalidated due to operational problems with the CFB boiler;

(I) Supplementary RATA information required under 40 CFR 75.59(a)(7), except that:

( I ) The applicable data elements under 40 CFR 75.59(a)(7)(ii)(A) through (T) and under 40 CFR 75.59(a)(7)(iii)(A) through (M) shall be reported for flow RATAs at circular or rectangular stacks (or ducts) in which angular compensation for yaw and/or pitch angles is used (i.e., EPA Method 2F or 2G in appendices A-1 and A-2 to 40 CFR part 60), with or without wall effects adjustments;

## **Attachment: Mercury Monitoring Provisions**

( 2 ) The applicable data elements under 40 CFR 75.59(a)(7)(ii)(A) through (T) and under 40 CFR 75.59(a)(7)(iii)(A) through (M) shall be reported for any flow RATA run at a circular stack in which EPA Method 2 in appendices A-1 and A-2 to 40 CFR part 60 is used and a wall effects adjustment factor is determined by direct measurement;

( 3 ) The data under 40 CFR 75.59(a)(7)(ii)(T) shall be reported for all flow RATAs at circular stacks in which EPA Method 2 in appendices A-1 and A-2 to 40 CFR part 60 is used and a default wall effects adjustment factor is applied; and

( 4 ) The data under 40 CFR 75.59(a)(7)(ix)(A) through (F) shall be reported for all flow RATAs at rectangular stacks or ducts in which Method 2 in appendices A-1 and A-2 to 40 CFR part 60 is used and a wall effects adjustment factor is applied.

(J) For units using sorbent trap monitoring systems, the hourly gas flow meter readings taken between the initial and final meter readings for the data collection period; and

(i) Ounces of Hg emitted during quarter and cumulative ounces of Hg emitted in the year-to-date (rounded to the nearest thousandth); and

(ii) Unit or stack operating hours for quarter, cumulative unit or stack operating hours for year-to-date; and

(iii) Reporting period heat input and cumulative, year-to-date heat input.

(2) *Compliance certification.* (i) The responsible official shall certify that the monitoring plan information in each quarterly electronic report ( *i.e.* , component and system identification codes, formulas, etc.) represent current operating conditions for the affected unit(s)

(ii) The responsible official shall submit and sign a compliance certification in support of each quarterly emissions monitoring report based on reasonable inquiry of those persons with primary responsibility for ensuring that all of the unit's emissions are correctly and fully monitored. The certification shall state that:

(A) The monitoring data submitted were recorded in accordance with the applicable requirements of this attachment, including the quality assurance procedures and specifications; and

(B) For all hours where data are substituted in accordance with 40 CFR 75.38(b), the permittee shall verify that the add-on emission controls were operating within the range of parameters listed in the quality-assurance plan for the unit (or that quality-assured SO<sub>2</sub> CEMS data were available to document proper operation of the emission controls), and that the substitute values do not systematically underestimate Hg emissions.

(3) *Additional reporting requirements.* The responsible official shall also comply with all of the quarterly reporting requirements in 40 CFR 40 CFR 75.64(d), (f), and (g).

## **Attachment: Mercury Monitoring Provisions**

### **Appendix A to Attachment—Specifications and Test Procedures**

#### **1. Installation and Measurement Location**

##### *1.1 Gas and Hg Monitors*

Following the procedures in section 8.1.1 of Performance Specification 2 in appendix B to 40 CFR part 60, install the pollutant concentration monitor or monitoring system at a location where the pollutant concentration and emission rate measurements are directly representative of the total emissions from the CFB boilers. Select a representative measurement point or path for the monitor probe(s) (or for the path from the transmitter to the receiver) such that the SO<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, and NO<sub>x</sub> concentration monitoring system or NO<sub>x</sub>-diluent CEMS (NO<sub>x</sub> pollutant concentration monitor and diluent gas monitor), Hg concentration monitoring system, or sorbent trap monitoring system will pass the relative accuracy test (see section 6 of this appendix).

It is recommended that monitor measurements be made at locations where the exhaust gas temperature is above the dew-point temperature. If the cause of failure to meet the relative accuracy tests is determined to be the measurement location, relocate the monitor probe(s).

##### **1.1.1 Point Monitors**

Locate the measurement point (1) within the centroidal area of the stack or duct cross section, or (2) no less than 1.0 meter from the stack or duct wall.

##### **1.1.2 Path Monitors**

Locate the measurement path (1) totally within the inner area bounded by a line 1.0 meter from the stack or duct wall, or (2) such that at least 70.0 percent of the path is within the inner 50.0 percent of the stack or duct cross-sectional area, or (3) such that the path is centrally located within any part of the centroidal area.

##### *1.2 Flow Monitors*

Install the flow monitor in a location that provides representative volumetric flow over all operating conditions. Such a location is one that provides an average velocity of the flue gas flow over the stack or duct cross section, provides a representative SO<sub>2</sub> emission rate (in lb/hr), and is representative of the pollutant concentration monitor location. Where the moisture content of the flue gas affects volumetric flow measurements, use the procedures in both EPA Reference Methods 1 and 4 of appendix A to 40 CFR part 60 to establish a proper location for the flow monitor. The DEQ recommends (but does not require) performing a flow profile study following the procedures in 40 CFR part 60, appendix A, method 1, sections 11.5 or 11.4 for each of the three operating or load levels indicated in section 6.5.2.1 of this appendix to determine the acceptability of the potential flow monitor location and to determine the number and location of flow sampling points

## **Attachment: Mercury Monitoring Provisions**

required to obtain a representative flow value. The procedure in 40 CFR part 60, appendix A, Test Method 1, section 11.5 may be used even if the flow measurement location is greater than or equal to 2 equivalent stack or duct diameters downstream or greater than or equal to 1/2 duct diameter upstream from a flow disturbance. If a flow profile study shows that cyclonic (or swirling) or stratified flow conditions exist at the potential flow monitor location that are likely to prevent the monitor from meeting the performance specifications of this attachment, then DEQ recommends either (1) selecting another location where there is no cyclonic (or swirling) or stratified flow condition, or (2) eliminating the cyclonic (or swirling) or stratified flow condition by straightening the flow, e.g., by installing straightening vanes. DEQ also recommends selecting flow monitor locations to minimize the effects of condensation, coating, erosion, or other conditions that could adversely affect flow monitor performance.

### **1.2.1 Acceptability of Monitor Location**

The installation of a flow monitor is acceptable if either (1) the location satisfies the minimum siting criteria of EPA Method 1 in appendix A to 40 CFR part 60 (i.e., the location is greater than or equal to eight stack or duct diameters downstream and two diameters upstream from a flow disturbance; or, if necessary, two stack or duct diameters downstream and one-half stack or duct diameter upstream from a flow disturbance), or (2) the results of a flow profile study, if performed, are acceptable (i.e., there are no cyclonic (or swirling) or stratified flow conditions), and the flow monitor also satisfies the performance specifications of this attachment. If the flow monitor is installed in a location that does not satisfy these physical criteria, but nevertheless the monitor achieves the performance specifications of this attachment, then the location is acceptable, notwithstanding the requirements of this section.

### **1.2.2 Alternative Monitoring Location**

Whenever the permittee successfully demonstrates that modifications to the exhaust duct or stack (such as installation of straightening vanes, modifications of ductwork, and the like) are necessary for the flow monitor to meet the performance specifications, the DEQ may approve an interim alternative flow monitoring methodology and an extension to the required certification date for the flow monitor.

Where no location exists that satisfies the physical siting criteria in section 1.2.1, where the results of flow profile studies performed at two or more alternative flow monitor locations are unacceptable, or where installation of a flow monitor in either the stack or the ducts is demonstrated to be technically infeasible, the permittee may petition the DEQ for an alternative method for monitoring flow.

## **2. Equipment Specifications**

### **2.1 Instrument Span and Range**

## Attachment: Mercury Monitoring Provisions

In implementing sections 2.1.1 through 2.1.6 of this appendix, set the measurement range for each parameter ( $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{CO}_2$ ,  $\text{O}_2$ , or flow rate) high enough to prevent full-scale exceedances from occurring, yet low enough to ensure good measurement accuracy and to maintain a high signal-to-noise ratio. To meet these objectives, select the range such that the majority of the readings obtained during typical unit operation are kept, to the extent practicable, between 20.0 and 80.0 percent of the full-scale range of the instrument. These guidelines do not apply to: (1)  $\text{SO}_2$  readings obtained during the combustion of very low sulfur fuel (as defined in 40 CFR 72.2); (2)  $\text{SO}_2$  or  $\text{NO}_x$  readings recorded on the high measurement range, for units with  $\text{SO}_2$  or  $\text{NO}_x$  emission controls and two span values, unless the emission controls are operated seasonally (for example, only during the ozone season); or (3)  $\text{SO}_2$  or  $\text{NO}_x$  readings less than 20.0 percent of full-scale on the low measurement range for a dual span unit, provided that the maximum expected concentration (MEC), low-scale span value, and low-scale range settings have been determined according to sections 2.1.1.2, 2.1.1.4(a), (b), and (g) of this appendix (for  $\text{SO}_2$ ), or according to sections 2.1.2.2, 2.1.2.4(a) and (f) of this appendix (for  $\text{NO}_x$ ).

### 2.1.1 $\text{SO}_2$ Pollutant Concentration Monitors

Determine, as indicated in sections 2.1.1.1 through 2.1.1.5 of this appendix the span value(s) and range(s) for an  $\text{SO}_2$  pollutant concentration monitor so that all potential and expected concentrations can be accurately measured and recorded. Note that if a unit exclusively combusts fuels that are very low sulfur fuels (as defined in 40 CFR 72.2), the  $\text{SO}_2$  monitor span requirements in 40 CFR 75.11(e)(3)(iv) apply in lieu of the requirements of this section.

#### 2.1.1.1 Maximum Potential Concentration

(a) Make an initial determination of the maximum potential concentration (MPC) of  $\text{SO}_2$  by using Equation A-1a or A-1b. Base the MPC calculation on the maximum percent sulfur and the minimum gross calorific value (GCV) for the highest-sulfur fuel to be burned. The maximum sulfur content and minimum GCV shall be determined from all available fuel sampling and analysis data for that fuel from the previous 12 months (minimum), excluding clearly anomalous fuel sampling values. If both the fuel sulfur content and the GCV are routinely determined from each fuel sample, the permittee may, as an alternative to using the highest individual percent sulfur and lowest individual GCV values in the MPC calculation, pair the sulfur content and GCV values from each sample analysis and calculate the ratio of percent sulfur to GCV (*i.e.*, %S/GCV) for each pair of values. If this option is selected, the MPC shall be calculated using the highest %S/GCV ratio in Equation A-1a or A-1b. If the responsible official certifies that the highest-sulfur fuel is never burned alone in the unit during normal operation but is always blended or co-fired with other fuel(s), the MPC may be calculated using a best estimate of the highest sulfur content and lowest gross calorific value expected for the blend or fuel mixture and inserting these values into Equation A-1a or A-1b. Derive the best estimate of the highest percent sulfur and lowest GCV for a blend or fuel mixture from weighted-average values based upon the historical composition of the blend or mixture in the previous 12 (or more) months. If insufficient representative fuel sampling data are



## Attachment: Mercury Monitoring Provisions

available to determine the maximum sulfur content and minimum GCV, use values from contract(s) for the fuel(s) that will be combusted by the unit in the MPC calculation.

$$MPC \text{ (or MEC)} = 11.32 \times 10^6 \left( \frac{\%S}{GCV} \right) \left( \frac{20.9 - \%O_{2w}}{20.9} \right) \quad (Eq. A-10)$$

or

$$MPC \text{ (or MEC)} = 66.93 \times 10^6 \left( \frac{\%S}{GCV} \right) \left( \frac{\%CO_{2w}}{100} \right) \quad (Eq. A-11)$$

Where,

MPC = Maximum potential concentration (ppm, wet basis). (To convert to dry basis, divide the MPC by 0.9.)

MEC = Maximum expected concentration (ppm, wet basis). (To convert to dry basis, divide the MEC by 0.9).

%S = Maximum sulfur content of fuel to be fired, wet basis, weight percent, as determined according to the applicable method in paragraph (c) of section 2.1.1.1.

%O<sub>2w</sub> = Minimum oxygen concentration, percent wet basis, under typical operating conditions.

%CO<sub>2w</sub> = Maximum carbon dioxide concentration, percent wet basis, under typical operating conditions.

GCV = Minimum gross calorific value of the fuel or blend to be combusted, based on historical fuel sampling and analysis data or, if applicable, based on the fuel contract specifications (Btu/lb). If based on fuel sampling and analysis, the GCV shall be determined according to the applicable method in paragraph (c) of section 2.1.1.1.

$11.32 \times 10^6$  = Oxygen-based conversion factor in Btu/lb (ppm)/%.

$66.93 \times 10^6$  = Carbon dioxide-based conversion factor in Btu/lb (ppm)/%.

Note: All percent values to be inserted in the equations of this section are to be expressed as a percentage, not a fractional value (e.g., 3, not .03).

(b) Alternatively, if a certified SO<sub>2</sub> CEMS is already installed, the permittee may make the initial MPC determination based upon quality-assured historical data recorded by the CEMS. For the purposes of this section, 2.1.1.1, a “certified” CEMS means a CEM system that has met the applicable certification requirements of either: This attachment, or 40 CFR part 60, or a State CEM program, or the source operating permit. If this option is chosen, the MPC shall be the maximum SO<sub>2</sub> concentration observed during the

## **Attachment: Mercury Monitoring Provisions**

previous 720 (or more) quality-assured monitor operating hours when combusting the highest-sulfur fuel (or highest-sulfur blend if fuels are always blended or co-fired) that is to be combusted in the unit or units monitored by the SO<sub>2</sub> monitor. For units with SO<sub>2</sub> emission controls, the certified SO<sub>2</sub> monitor used to determine the MPC must be located at or before the control device inlet. Report the MPC and the method of determination in the monitoring plan required under 40 CFR 75.53. Note that the initial MPC value is subject to periodic review under section 2.1.1.5 of this appendix. If an MPC value is found to be either inappropriately high or low, the MPC shall be adjusted in accordance with section 2.1.1.5, and corresponding span and range adjustments shall be made, if necessary.

(c) When performing fuel sampling to determine the MPC, use ASTM Methods: ASTM D3177-02 (Reapproved 2007), Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke; ASTM D4239-02, Standard Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion Methods; ASTM D4294-98, Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy-Dispersive X-ray Fluorescence Spectrometry; ASTM D1552-01, Standard Test Method for Sulfur in Petroleum Products (High-Temperature Method); ASTM D129-00, Standard Test Method for Sulfur in Petroleum Products (General Bomb Method); ASTM D2622-98, Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry, for sulfur content of solid or liquid fuels; ASTM D3176-89 (Reapproved 2002), Standard Practice for Ultimate Analysis of Coal and Coke; ASTM D240-00, Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter; or ASTM D5865-01a, Standard Test Method for Gross Calorific Value of Coal and Coke (all incorporated by reference under 40 CFR 75.6).

### **2.1.1.2 Maximum Expected Concentration**

(a) Make an initial determination of the maximum expected concentration (MEC) of SO<sub>2</sub> whenever: (a) SO<sub>2</sub> emission controls are used; or (b) both high-sulfur and low-sulfur fuels (e.g., high-sulfur coal and low-sulfur coal or different grades of fuel oil) or high-sulfur and low-sulfur fuel blends are combusted as primary or backup fuels in a unit without SO<sub>2</sub> emission controls. For units with SO<sub>2</sub> emission controls, use Equation A-2 to make the initial MEC determination. When high-sulfur and low-sulfur fuels or blends are burned as primary or backup fuels in a unit without SO<sub>2</sub> controls, use Equation A-1a or A-1b to calculate the initial MEC value for each fuel or blend, except for: (1) the highest-sulfur fuel or blend (for which the MPC was previously calculated in section 2.1.1.1 of this appendix); (2) fuels or blends that are very low sulfur fuels (as defined in 40 CFR 72.2); or (3) fuels or blends that are used only for unit startup. Each initial MEC value shall be documented in the monitoring plan required under 40 CFR 75.53. Note that each initial MEC value is subject to periodic review under section 2.1.1.5 of this appendix. If an MEC value is found to be either inappropriately high or low, the MEC shall be adjusted in accordance with section 2.1.1.5, and corresponding span and range adjustments shall be made, if necessary.

## Attachment: Mercury Monitoring Provisions

(b) For each MEC determination, substitute into Equation A-1a or A-1b the highest sulfur content and minimum GCV value for that fuel or blend, based upon all available fuel sampling and analysis results from the previous 12 months (or more), or, if fuel sampling data are unavailable, based upon fuel contract(s).

(c) Alternatively, if a certified SO<sub>2</sub> CEMS is already installed, the permittee may make the initial MEC determination(s) based upon historical monitoring data. For the purposes of this section, 2.1.1.2, a "certified" CEMS means a CEM system that has met the applicable certification requirements of either: This attachment, or 40 CFR part 60, or a State CEM program, or the source operating permit. If this option is chosen for a unit with SO<sub>2</sub> emission controls, the MEC shall be the maximum SO<sub>2</sub> concentration measured downstream of the control device outlet by the CEMS over the previous 720 (or more) quality-assured monitor operating hours with the unit and the control device both operating normally. For units that burn high- and low-sulfur fuels or blends as primary and backup fuels and have no SO<sub>2</sub> emission controls, the MEC for each fuel shall be the maximum SO<sub>2</sub> concentration measured by the CEMS over the previous 720 (or more) quality-assured monitor operating hours in which that fuel or blend was the only fuel being burned in the unit.

$$MEC = MPC \left( \frac{100 - RE}{100} \right) \quad (Eq. A-2)$$

Where:

MEC = Maximum expected concentration (ppm).

MPC = Maximum potential concentration (ppm), as determined by Eq. A-1a or A-1b in section 2.1.1.1 of this appendix.

RE = Expected average design removal efficiency of control equipment (%).

### 2.1.1.3 Span Value(s) and Range(s)

Determine the high span value and the high full-scale range of the SO<sub>2</sub> monitor as follows. (Note: For purposes of this attachment, the high span and range refer, respectively, either to the span and range of a single span unit or to the high span and range of a dual span unit.) The high span value shall be obtained by multiplying the MPC by a factor no less than 1.00 and no greater than 1.25. Round the span value upward to the next highest multiple of 100 ppm. If the SO<sub>2</sub> span concentration is ≤ 500 ppm, the span value may either be rounded upward to the next highest multiple of 10 ppm, or to the next highest multiple of 100 ppm. The high span value shall be used to determine concentrations of the calibration gases required for daily calibration error checks and linearity tests. Select the full-scale range of the instrument to be consistent with section 2.1 of this appendix and to be greater than or equal to the span value. Report the full-scale range setting and calculations of the MPC and span in the monitoring plan for the unit. Note that for certain applications, a second (low) SO<sub>2</sub> span and range may be

## **Attachment: Mercury Monitoring Provisions**

required (see section 2.1.1.4 of this appendix). If an existing State, local, or federal requirement for span of an SO<sub>2</sub> pollutant concentration monitor requires or allows the use of a span value lower than that required by this section or by section 2.1.1.4 of this appendix, the State, local, or federal span value may be used if a satisfactory explanation is included in the monitoring plan, unless span and/or range adjustments become necessary in accordance with section 2.1.1.5 of this appendix. Span values higher than those required by either this section or section 2.1.1.4 of this appendix must be approved by the DEQ.

### **2.1.1.4 Dual Span and Range Requirements**

For most units, the high span value based on the MPC, as determined under section 2.1.1.3 of this appendix will suffice to measure and record SO<sub>2</sub> concentrations (unless span and/or range adjustments become necessary in accordance with section 2.1.1.5 of this appendix). In some instances, however, a second (low) span value based on the MEC may be required to ensure accurate measurement of all possible or expected SO<sub>2</sub> concentrations. To determine whether two SO<sub>2</sub> span values are required, proceed as follows:

(a) For units with SO<sub>2</sub> emission controls, compare the MEC from section 2.1.1.2 of this appendix to the high full-scale range value from section 2.1.1.3 of this appendix. If the MEC is  $\geq 20.0$  percent of the high range value, then the high span value and range determined under section 2.1.1.3 of this appendix are sufficient. If the MEC is  $< 20.0$  percent of the high range value, then a second (low) span value is required.

(b) For units that combust high- and low-sulfur primary and backup fuels (or blends) and have no SO<sub>2</sub> controls, compare the high range value from section 2.1.1.3 of this appendix (for the highest-sulfur fuel or blend) to the MEC value for each of the other fuels or blends, as determined under section 2.1.1.2 of this appendix. If all of the MEC values are  $\geq 20.0$  percent of the high range value, the high span and range determined under section 2.1.1.3 of this appendix are sufficient, regardless of which fuel or blend is burned in the unit. If any MEC value is  $< 20.0$  percent of the high range value, then a second (low) span value must be used when that fuel or blend is combusted.

(c) When two SO<sub>2</sub> spans are required, the permittee may either use a single SO<sub>2</sub> analyzer with a dual range (i.e., low- and high-scales) or two separate SO<sub>2</sub> analyzers connected to a common sample probe and sample interface. Alternatively, if RATAs are performed and passed on both measurement ranges, the permittee may use two separate SO<sub>2</sub> analyzers connected to separate probes and sample interfaces. For units with SO<sub>2</sub> emission controls, the permittee may use a low range analyzer and a default high range value, as described in paragraph (f) of this section, in lieu of maintaining and quality assuring a high-scale range. Other monitor configurations are subject to the approval of the DEQ.

(d) The permittee shall designate the monitoring systems and components in the monitoring plan under 40 CFR 75.53 as follows: when a single probe and sample

## Attachment: Mercury Monitoring Provisions

interface are used, either designate the low and high monitor ranges as separate SO<sub>2</sub> components of a single, primary SO<sub>2</sub> monitoring system; designate the low and high monitor ranges as the SO<sub>2</sub> components of two separate, primary SO<sub>2</sub> monitoring systems; designate the normal monitor range as a primary monitoring system and the other monitor range as a non-redundant backup monitoring system; or, when a single, dual-range SO<sub>2</sub> analyzer is used, designate the low and high ranges as a single SO<sub>2</sub> component of a primary SO<sub>2</sub> monitoring system (if this option is selected, use a special dual-range component type code, as specified by the DEQ, to satisfy the requirements of 40 CFR 75.53(e)(1)(iv)(D)). When two SO<sub>2</sub> analyzers are connected to separate probes and sample interfaces, designate the analyzers as the SO<sub>2</sub> components of two separate, primary SO<sub>2</sub> monitoring systems. For units with SO<sub>2</sub> controls, if the default high range value is used, designate the low range analyzer as the SO<sub>2</sub> component of a primary SO<sub>2</sub> monitoring system. Do not designate the default high range as a monitoring system or component. Other component and system designations are subject to approval by the DEQ. Note that the component and system designations for redundant backup monitoring systems shall be the same as for primary monitoring systems.

(e) Each monitoring system designated as primary or redundant backup shall meet the initial certification and quality assurance requirements for primary monitoring systems in 40 CFR 75.20(c) or 40 CFR 75.20(d)(1), as applicable, and appendices A and B to this attachment, with one exception: relative accuracy test audits (RATAs) are required only on the normal range (for units with SO<sub>2</sub> emission controls, the low range is considered normal). Each monitoring system designated as a non-redundant backup shall meet the applicable quality assurance requirements in 40 CFR 75.20(d)(2).

(f) For dual span units with SO<sub>2</sub> emission controls, the permittee may, as an alternative to maintaining and quality assuring a high monitor range, use a default high range value. If this option is chosen, the permittee shall report a default SO<sub>2</sub> concentration of 200 percent of the MPC for each unit operating hour in which the full-scale of the low range SO<sub>2</sub> analyzer is exceeded.

(g) The high span value and range shall be determined in accordance with section 2.1.1.3 of this appendix. The low span value shall be obtained by multiplying the MEC by a factor no less than 1.00 and no greater than 1.25, and rounding the result upward to the next highest multiple of 10 ppm (or 100 ppm, as appropriate). For units that burn high- and low-sulfur primary and backup fuels or blends and have no SO<sub>2</sub> emission controls, select, as the basis for calculating the appropriate low span value and range, the fuel-specific MEC value closest to 20.0 percent of the high full-scale range value (from paragraph (b) of this section). The low range must be greater than or equal to the low span value, and the required calibration gases must be selected based on the low span value. However, if the default high range option in paragraph (f) of this section is selected, the full-scale of the low measurement range shall not exceed five times the MEC value (where the MEC is rounded upward to the next highest multiple of 10 ppm). For units with two SO<sub>2</sub> spans, use the low range whenever the SO<sub>2</sub> concentrations are expected to be consistently below 20.0 percent of the high full-scale range value, i.e., when the MEC of the fuel or blend being combusted is less than 20.0 percent of the high

## **Attachment: Mercury Monitoring Provisions**

full-scale range value. When the full-scale of the low range is exceeded, the high range shall be used to measure and record the SO<sub>2</sub> concentrations; or, if applicable, the default high range value in paragraph (f) of this section shall be reported for each hour of the full-scale exceedance.

### **2.1.1.5 Adjustment of Span and Range**

For each CFB boiler, the permittee shall make a periodic evaluation of the MPC, MEC, span, and range values for each SO<sub>2</sub> monitor (at a minimum, an annual evaluation is required) and shall make any necessary span and range adjustments, with corresponding monitoring plan updates, as described in paragraphs (a), (b), and (c) of this section. Span and range adjustments may be required, for example, as a result of changes in the fuel supply, changes in the manner of operation of the unit, or installation or removal of emission controls. In implementing the provisions in paragraphs (a) and (b) of this section, SO<sub>2</sub> data recorded during short-term, non-representative process operating conditions (e.g., a trial burn of a different type of fuel) shall be excluded from consideration. The permittee shall keep the results of the most recent span and range evaluation on-site, in a format suitable for inspection. Make each required span or range adjustment no later than 45 days after the end of the quarter in which the need to adjust the span or range is identified, except that up to 90 days after the end of that quarter may be taken to implement a span adjustment if the calibration gases currently being used for daily calibration error tests and linearity checks are unsuitable for use with the new span value.

(a) If the fuel supply, the composition of the fuel blend(s), the emission controls, or the manner of operation change such that the maximum expected or potential concentration changes significantly, adjust the span and range setting to assure the continued accuracy of the monitoring system. A "significant" change in the MPC or MEC means that the guidelines in section 2.1 of this appendix can no longer be met, as determined by either a periodic evaluation by the permittee or from the results of an audit by the DEQ. The permittee should evaluate whether any planned changes in operation of the unit may affect the concentration of emissions being emitted from the unit or stack and should plan any necessary span and range changes needed to account for these changes, so that they are made in as timely a manner as practicable to coordinate with the operational changes. Determine the adjusted span(s) using the procedures in sections 2.1.1.3 and 2.1.1.4 of this appendix (as applicable). Select the full-scale range(s) of the instrument to be greater than or equal to the new span value(s) and to be consistent with the guidelines of section 2.1 of this appendix.

(b) Whenever a full-scale range is exceeded during a quarter and the exceedance is not caused by a monitor out-of-control period, proceed as follows:

(1) For exceedances of the high range, report 200.0 percent of the current full-scale range as the hourly SO<sub>2</sub> concentration for each hour of the full-scale exceedance and make appropriate adjustments to the MPC, span, and range to prevent future full-scale exceedances.

## **Attachment: Mercury Monitoring Provisions**

(2) For units with two SO<sub>2</sub> spans and ranges, if the low range is exceeded, no further action is required, provided that the high range is available and its most recent calibration error test and linearity check have not expired. However, if either of these quality assurance tests has expired and the high range is not able to provide quality assured data at the time of the low range exceedance or at any time during the continuation of the exceedance, report the MPC as the SO<sub>2</sub> concentration until the readings return to the low range or until the high range is able to provide quality assured data (unless the reason that the high-scale range is not able to provide quality assured data is because the high-scale range has been exceeded; if the high-scale range is exceeded follow the procedures in paragraph (b)(1) of this section).

(c) Whenever changes are made to the MPC, MEC, full-scale range, or span value of the SO<sub>2</sub> monitor, as described in paragraphs (a) or (b) of this section, record and report (as applicable) the new full-scale range setting, the new MPC or MEC and calculations of the adjusted span value in an updated monitoring plan. The monitoring plan update shall be made in the quarter in which the changes become effective. In addition, record and report the adjusted span as part of the records for the daily calibration error test and linearity check specified by appendix B to this attachment. Whenever the span value is adjusted, use calibration gas concentrations that meet the requirements of section 5.1 of this appendix, based on the adjusted span value. When a span adjustment is so significant that the calibration gases currently being used for daily calibration error tests and linearity checks are unsuitable for use with the new span value, then a diagnostic linearity test using the new calibration gases must be performed and passed. Use the data validation procedures in 40 CFR 75.20(b)(3), beginning with the hour in which the span is changed.

### **2.1.2 NO<sub>x</sub> Pollutant Concentration Monitors**

Determine, as indicated in sections 2.1.2.1 through 2.1.2.5 of this appendix, the span and range value(s) for the NO<sub>x</sub> pollutant concentration monitor so that all expected NO<sub>x</sub> concentrations can be determined and recorded accurately.

#### **2.1.2.1 Maximum Potential Concentration**

(a) The maximum potential concentration (MPC) of NO<sub>x</sub> for each CFB boiler shall be based upon whichever fuel or blend combusted in the unit produces the highest level of NO<sub>x</sub> emissions. For the purposes of this section, 2.1.2.1, and section 2.1.2.2 of this appendix, a “blend” means a frequently-used fuel mixture having a consistent composition (e.g., an oil and gas mixture where the relative proportions of the two fuels vary by no more than 10%, on average). Make an initial determination of the MPC using the appropriate option as follows:

Option 1: Use 800 ppm for coal-fired units as the maximum potential concentration of NO<sub>x</sub> (if an MPC of 1600 ppm for coal-fired units, that value may still be used, provided that the guidelines of section 2.1 of this appendix are met).

## **Attachment: Mercury Monitoring Provisions**

Option 2: Use the specific values based on boiler type and fuel combusted, listed in Table 2-1.

Option 3: Use NO<sub>x</sub> emission test results;

Option 4: Use historical CEM data over the previous 720 (or more) unit operating hours when combusting the fuel or blend with the highest NO<sub>x</sub> emission rate; or

Option 5: If a reliable estimate of the uncontrolled NO<sub>x</sub> emissions from the unit is available from the manufacturer, the estimated value may be used.

(b) For the purpose of providing substitute data during NO<sub>x</sub> missing data periods in accordance with 40 CFR 75.31 and 75.33 and as required elsewhere under 40 CFR part 75, the permittee shall also calculate the maximum potential NO<sub>x</sub> emission rate (MER), in lb/mmBtu, by substituting the MPC for NO<sub>x</sub> in conjunction with the minimum expected CO<sub>2</sub> or maximum O<sub>2</sub> concentration (under all unit operating conditions except for unit startup, shutdown, and upsets) and the appropriate F-factor into the applicable equation in appendix F to this attachment. The diluent cap value of 5.0 percent CO<sub>2</sub> (or 14.0 percent O<sub>2</sub>) for boilers or 1.0 percent CO<sub>2</sub> (or 19.0 percent O<sub>2</sub>) for combustion turbines may be used in the NO<sub>x</sub> MER calculation. As a second alternative, when the NO<sub>x</sub> MPC is determined from emission test results or from historical CEM data, as described in paragraphs (a), (d) and (e) of this section, quality-assured diluent gas (i.e., O<sub>2</sub> or CO<sub>2</sub>) data recorded concurrently with the MPC may be used to calculate the MER.

(c) Report the method of determining the initial MPC and the calculation of the maximum potential NO<sub>x</sub> emission rate in the monitoring plan for the unit. Note that whichever MPC option in paragraph 2.1.2.1(a) of this appendix is selected, the initial MPC value is subject to periodic review under section 2.1.2.5 of this appendix. If an MPC value is found to be either inappropriately high or low, the MPC shall be adjusted in accordance with section 2.1.2.5, and corresponding span and range adjustments shall be made, if necessary.

(d) For units with add-on NO<sub>x</sub> controls (whether or not the unit is equipped with low-NO<sub>x</sub> burner technology), or for units equipped with dry low-NO<sub>x</sub> (DLN) technology, NO<sub>x</sub> emission testing may only be used to determine the MPC if testing can be performed either upstream of the add-on controls or during a time or season when the add-on controls are not in operation or when the DLN controls are not in the premixed (low-NO<sub>x</sub>) mode. If NO<sub>x</sub> emission testing is performed, use the following guidelines. Use EPA Method 7E from appendix A to 40 CFR part 60 to measure total NO<sub>x</sub> concentration. (Note: EPA Method 20 from appendix A to 40 CFR part 60 may be used for gas turbines, instead of Method 7E.) Operate the unit, or group of units sharing a common stack, at the minimum safe and stable load, the normal load, and the maximum load. If the normal load and maximum load are identical, an intermediate level need not be tested. Operate at the highest excess O<sub>2</sub> level expected under normal operating conditions. Make at least three runs of 20 minutes (minimum) duration with three traverse points per run at each



## Attachment: Mercury Monitoring Provisions

operating condition. Select the highest point NO<sub>x</sub> concentration from all test runs as the MPC for NO<sub>x</sub>.

(e) If historical CEM data are used to determine the MPC, the data must, for uncontrolled units or units equipped with low-NO<sub>x</sub> burner technology and no other NO<sub>x</sub> controls, represent a minimum of 720 quality-assured monitor operating hours from the NO<sub>x</sub> component of a certified monitoring system, obtained under various operating conditions including the minimum safe and stable load, normal load (including periods of high excess air at normal load), and maximum load. For the purposes of this section, 2.1.2.1, a “certified” CEMS means a CEM system that has met the applicable certification requirements of either: this attachment, or 40 CFR part 60, or a State CEM program, or the source operating permit. For a unit with add-on NO<sub>x</sub> controls (whether or not the unit is equipped with low-NO<sub>x</sub> burner technology), or for a unit equipped with dry low-NO<sub>x</sub> (DLN) technology, historical CEM data may only be used to determine the MPC if the 720 quality-assured monitor operating hours of CEM data are collected upstream of the add-on controls or if the 720 hours of data include periods when the add-on controls are not in operation or when the DLN controls are not in the premixed (low-NO<sub>x</sub> mode). For units that do not produce electrical or thermal output, the data must represent the full range of normal process operation. The highest hourly NO<sub>x</sub> concentration in ppm shall be the MPC.

**Table 2–1—Maximum Potential Concentration for NO<sub>x</sub>—Coal-Fired Units**

Unit type	Maximum potential concentration for NO <sub>x</sub> (ppm)
Tangentially-fired dry bottom and fluidized bed	460
Wall-fired dry bottom, turbo-fired dry bottom, stokers	675
Roof-fired (vertically-fired) dry bottom, cell burners, arch-fired	975
Cyclone, wall-fired wet bottom, wet bottom turbo-fired	1200
Others	( <sup>1</sup> )

<sup>1</sup>As approved by the DEQ.

### 2.1.2.2 Maximum Expected Concentration

(a) Make an initial determination of the maximum expected concentration (MEC) of NO<sub>x</sub> during normal operation for affected units with add-on NO<sub>x</sub> controls of any kind (e.g., steam injection, water injection, SCR, or SNCR) and for turbines that use dry low-NO<sub>x</sub> technology. Determine a separate MEC value for each type of fuel (or blend) combusted in the unit, except for fuels that are only used for unit startup and/or flame stabilization.

## **Attachment: Mercury Monitoring Provisions**

Calculate the MEC of NO<sub>x</sub> using Equation A-2, if applicable, inserting the maximum potential concentration, as determined using the procedures in section 2.1.2.1 of this appendix. Where Equation A-2 is not applicable, set the MEC either by: (1) measuring the NO<sub>x</sub> concentration using the testing procedures in this section; (2) using historical CEM data over the previous 720 (or more) quality-assured monitor operating hours; or (3) if the unit has add-on NO<sub>x</sub> controls or uses dry low NO<sub>x</sub> technology, and has a federally-enforceable permit limit for NO<sub>x</sub> concentration, the permit limit may be used as the MEC. Include in the monitoring plan for the unit each MEC value and the method by which the MEC was determined. Note that each initial MEC value is subject to periodic review under section 2.1.2.5 of this appendix. If an MEC value is found to be either inappropriately high or low, the MEC shall be adjusted in accordance with section 2.1.2.5, and corresponding span and range adjustments shall be made, if necessary.

(b) If NO<sub>x</sub> emission testing is used to determine the MEC value(s), the MEC for each type of fuel (or blend) shall be based upon testing at minimum load, normal load, and maximum load. At least three tests of 20 minutes (minimum) duration, using at least three traverse points, shall be performed at each load, using EPA Method 7E from appendix A to 40 CFR part 60. The test must be performed at a time when all NO<sub>x</sub> control devices and methods used to reduce NO<sub>x</sub> emissions (if applicable) are operating properly. The testing shall be conducted downstream of all NO<sub>x</sub> controls. The highest point NO<sub>x</sub> concentration (e.g., the highest one-minute average) recorded during any of the test runs shall be the MEC.

(c) If historical CEM data are used to determine the MEC value(s), the MEC for each type of fuel shall be based upon 720 (or more) hours of quality-assured data from the NO<sub>x</sub> component of a certified monitoring system representing the entire load range under stable operating conditions. For the purposes of this section, 2.1.2.2, a “certified” CEMS means a CEM system that has met the applicable certification requirements of either: this attachment, or 40 CFR part 60, or a State CEM program, or the source operating permit. The data base for the MEC shall not include any CEM data recorded during unit startup, shutdown, or malfunction or (for units with add-on NO<sub>x</sub> controls or turbines using dry low NO<sub>x</sub> technology) during any NO<sub>x</sub> control device malfunctions or outages. All NO<sub>x</sub> control devices and methods used to reduce NO<sub>x</sub> emissions (if applicable) must be operating properly during each hour. The CEM data shall be collected downstream of all NO<sub>x</sub> controls. For each type of fuel, the highest of the 720 (or more) quality-assured hourly average NO<sub>x</sub> concentrations recorded by the CEMS shall be the MEC.

### **2.1.2.3 Span Value(s) and Range(s)**

(a) Determine the high span value of the NO<sub>x</sub> monitor as follows. The high span value shall be obtained by multiplying the MPC by a factor no less than 1.00 and no greater than 1.25. Round the span value upward to the next highest multiple of 100 ppm. If the NO<sub>x</sub> span concentration is ≤500 ppm, the span value may either be rounded upward to the next highest multiple of 10 ppm, or to the next highest multiple of 100 ppm. The high span value shall be used to determine the concentrations of the calibration gases required

## **Attachment: Mercury Monitoring Provisions**

for daily calibration error checks and linearity tests. Note that for certain applications, a second (low) NO<sub>x</sub> span and range may be required (see section 2.1.2.4 of this appendix).

(b) If an existing State, local, or federal requirement for span of a NO<sub>x</sub> pollutant concentration monitor requires or allows the use of a span value lower than that required by this section or by section 2.1.2.4 of this appendix, the State, local, or federal span value may be used, where a satisfactory explanation is included in the monitoring plan, unless span and/or range adjustments become necessary in accordance with section 2.1.2.5 of this appendix. Span values higher than required by this section or by section 2.1.2.4 of this appendix must be approved by the DEQ.

(c) Select the full-scale range of the instrument to be consistent with section 2.1 of this appendix and to be greater than or equal to the high span value. Include the full-scale range setting and calculations of the MPC and span in the monitoring plan for the unit.

### **2.1.2.4 Dual Span and Range Requirements**

For most units, the high span value based on the MPC, as determined under section 2.1.2.3 of this appendix will suffice to measure and record NO<sub>x</sub> concentrations (unless span and/or range adjustments must be made in accordance with section 2.1.2.5 of this appendix). In some instances, however, a second (low) span value based on the MEC may be required to ensure accurate measurement of all expected and potential NO<sub>x</sub> concentrations. To determine whether two NO<sub>x</sub> spans are required, proceed as follows:

(a) Compare the MEC value(s) determined in section 2.1.2.2 of this appendix to the high full-scale range value determined in section 2.1.2.3 of this appendix. If the MEC values for all fuels (or blends) are  $\geq 20.0$  percent of the high range value, the high span and range values determined under section 2.1.2.3 of this appendix are sufficient, irrespective of which fuel or blend is combusted in the unit. If any of the MEC values is  $< 20.0$  percent of the high range value, two spans (low and high) are required, one based on the MPC and the other based on the MEC.

(b) When two NO<sub>x</sub> spans are required, the permittee may either use a single NO<sub>x</sub> analyzer with a dual range (low-and high-scales) or two separate NO<sub>x</sub> analyzers connected to a common sample probe and sample interface. Two separate NO<sub>x</sub> analyzers connected to separate probes and sample interfaces may be used if RATAs are passed on both ranges. For units with add-on NO<sub>x</sub> emission controls (e.g., steam injection, water injection, SCR, or SNCR) or units equipped with dry low-NO<sub>x</sub> technology, the permittee may use a low range analyzer and a “default high range value,” as described in paragraph 2.1.2.4(e) of this section, in lieu of maintaining and quality assuring a high-scale range. Other monitor configurations are subject to the approval of the DEQ.

(c) The permittee shall designate the monitoring systems and components in the monitoring plan under 40 CFR 75.53 as follows: when a single probe and sample interface are used, either designate the low and high ranges as separate NO<sub>x</sub> components of a single, primary NO<sub>x</sub> monitoring system; designate the low and high ranges as the

## **Attachment: Mercury Monitoring Provisions**

NO<sub>x</sub> components of two separate, primary NO<sub>x</sub> monitoring systems; designate the normal range as a primary monitoring system and the other range as a non-redundant backup monitoring system; or, when a single, dual-range NO<sub>x</sub> analyzer is used, designate the low and high ranges as a single NO<sub>x</sub> component of a primary NO<sub>x</sub> monitoring system (if this option is selected, use a special dual-range component type code, as specified by the DEQ, to satisfy the requirements of 40 CFR 75.53(e)(1)(iv)(D)). When two NO<sub>x</sub> analyzers are connected to separate probes and sample interfaces, designate the analyzers as the NO<sub>x</sub> components of two separate, primary NO<sub>x</sub> monitoring systems. For units with add-on NO<sub>x</sub> controls or units equipped with dry low-NO<sub>x</sub> technology, if the default high range value is used, designate the low range analyzer as the NO<sub>x</sub> component of the primary NO<sub>x</sub> monitoring system. Do not designate the default high range as a monitoring system or component. Other component and system designations are subject to approval by the DEQ. Note that the component and system designations for redundant backup monitoring systems shall be the same as for primary monitoring systems.

(d) Each monitoring system designated as primary or redundant backup shall meet the initial certification and quality assurance requirements in 40 CFR 75.20(c) (for primary monitoring systems), in 40 CFR 75.20(d)(1) (for redundant backup monitoring systems) and appendices A and B to this attachment, with one exception: relative accuracy test audits (RATAs) are required only on the normal range (for dual span units with add-on NO<sub>x</sub> emission controls, the low range is considered normal). Each monitoring system designated as non-redundant backup shall meet the applicable quality assurance requirements in 40 CFR 75.20(d)(2).

(e) For dual span units with add-on NO<sub>x</sub> emission controls (e.g., steam injection, water injection, SCR, or SNCR), or, for units that use dry low NO<sub>x</sub> technology, the permittee may, as an alternative to maintaining and quality assuring a high monitor range, use a default high range value. If this option is chosen, the permittee shall report a default value of 200.0 percent of the MPC for each unit operating hour in which the full-scale of the low range NO<sub>x</sub> analyzer is exceeded.

(f) The high span and range shall be determined in accordance with section 2.1.2.3 of this appendix. The low span value shall be 100.0 to 125.0 percent of the MEC, rounded up to the next highest multiple of 10 ppm (or 100 ppm, if appropriate). If more than one MEC value (as determined in section 2.1.2.2 of this appendix) is <20.0 percent of the high full-scale range value, the low span value shall be based upon whichever MEC value is closest to 20.0 percent of the high range value. The low range must be greater than or equal to the low span value, and the required calibration gases for the low range must be selected based on the low span value. However, if the default high range option in paragraph (e) of this section is selected, the full-scale of the low measurement range shall not exceed five times the MEC value (where the MEC is rounded upward to the next highest multiple of 10 ppm). For units with two NO<sub>x</sub> spans, use the low range whenever NO<sub>x</sub> concentrations are expected to be consistently <20.0 percent of the high range value, i.e., when the MEC of the fuel being combusted is <20.0 percent of the high range value. When the full-scale of the low range is exceeded, the high range shall be used to measure

## **Attachment: Mercury Monitoring Provisions**

and record the NO<sub>x</sub> concentrations; or, if applicable, the default high range value in paragraph (e) of this section shall be reported for each hour of the full-scale exceedance.

### **2.1.2.5 Adjustment of Span and Range**

For each CFB boiler, the permittee shall make a periodic evaluation of the MPC, MEC, span, and range values for each NO<sub>x</sub> monitor (at a minimum, an annual evaluation is required) and shall make any necessary span and range adjustments, with corresponding monitoring plan updates, as described in paragraphs (a), (b), and (c) of this section. Span and range adjustments may be required, for example, as a result of changes in the fuel supply, changes in the manner of operation of the unit, or installation or removal of emission controls. In implementing the provisions in paragraphs (a) and (b) of this section, note that NO<sub>x</sub> data recorded during short-term, non-representative operating conditions (e.g., a trial burn of a different type of fuel) shall be excluded from consideration. The permittee shall keep the results of the most recent span and range evaluation on-site, in a format suitable for inspection. Make each required span or range adjustment no later than 45 days after the end of the quarter in which the need to adjust the span or range is identified, except that up to 90 days after the end of that quarter may be taken to implement a span adjustment if the calibration gases currently being used for daily calibration error tests and linearity checks are unsuitable for use with the new span value.

(a) If the fuel supply, emission controls, or other process parameters change such that the maximum expected concentration or the maximum potential concentration changes significantly, adjust the NO<sub>x</sub> pollutant concentration span(s) and (if necessary) monitor range(s) to assure the continued accuracy of the monitoring system. A “significant” change in the MPC or MEC means that the guidelines in section 2.1 of this appendix can no longer be met, as determined by either a periodic evaluation by the permittee or from the results of an audit by the DEQ. The permittee should evaluate whether any planned changes in operation of the unit or stack may affect the concentration of emissions being emitted from the unit and should plan any necessary span and range changes needed to account for these changes, so that they are made in as timely a manner as practicable to coordinate with the operational changes. An example of a change that may require a span and range adjustment is the installation of low-NO<sub>x</sub> burner technology on a previously uncontrolled unit. Determine the adjusted span(s) using the procedures in section 2.1.2.3 or 2.1.2.4 of this appendix (as applicable). Select the full-scale range(s) of the instrument to be greater than or equal to the adjusted span value(s) and to be consistent with the guidelines of section 2.1 of this appendix.

(b) Whenever a full-scale range is exceeded during a quarter and the exceedance is not caused by a monitor out-of-control period, proceed as follows:

(1) For exceedances of the high range, report 200.0 percent of the current full-scale range as the hourly NO<sub>x</sub> concentration for each hour of the full-scale exceedance and make appropriate adjustments to the MPC, span, and range to prevent future full-scale exceedances.

## **Attachment: Mercury Monitoring Provisions**

(2) For units with two NO<sub>x</sub> spans and ranges, if the low range is exceeded, no further action is required, provided that the high range is available and its most recent calibration error test and linearity check have not expired. However, if either of these quality assurance tests has expired and the high range is not able to provide quality assured data at the time of the low range exceedance or at any time during the continuation of the exceedance, report the MPC as the NO<sub>x</sub> concentration until the readings return to the low range or until the high range is able to provide quality assured data (unless the reason that the high-scale range is not able to provide quality assured data is because the high-scale range has been exceeded; if the high-scale range is exceeded, follow the procedures in paragraph (b)(1) of this section).

(c) Whenever changes are made to the MPC, MEC, full-scale range, or span value of the NO<sub>x</sub> monitor as described in paragraphs (a) and (b) of this section, record and report (as applicable) the new full-scale range setting, the new MPC or MEC, maximum potential NO<sub>x</sub> emission rate, and the adjusted span value in an updated monitoring plan for the unit. The monitoring plan update shall be made in the quarter in which the changes become effective. In addition, record and report the adjusted span as part of the records for the daily calibration error test and linearity check required by appendix B to this attachment. Whenever the span value is adjusted, use calibration gas concentrations that meet the requirements of section 5.1 of this appendix, based on the adjusted span value. When a span adjustment is significant enough that the calibration gases currently being used for daily calibration error tests and linearity checks are unsuitable for use with the new span value, a diagnostic linearity test using the new calibration gases must be performed and passed. Use the data validation procedures in 40 CFR 75.20(b)(3), beginning with the hour in which the span is changed.

### **2.1.3 CO<sub>2</sub> and O<sub>2</sub> Monitors**

\* \* \* If a dual-range or auto ranging diluent analyzer is installed, the analyzer may be represented in the monitoring plan as a single component, using a special component type code specified by the DEQ to satisfy the requirements of 40 CFR 75.53(e)(1)(iv)(D).

### **2.1.3 CO<sub>2</sub> and O<sub>2</sub> Monitors**

For an O<sub>2</sub> monitor (including O<sub>2</sub> monitors used to measure CO<sub>2</sub> emissions or percentage moisture), select a span value between 15.0 and 25.0 percent O<sub>2</sub>. For a CO<sub>2</sub> monitor installed on a boiler, select a span value between 14.0 and 20.0 percent CO<sub>2</sub>. For a CO<sub>2</sub> monitor installed on a combustion turbine, an alternative span value between 6.0 and 14.0 percent CO<sub>2</sub> may be used. An alternative CO<sub>2</sub> span value below 6.0 percent may be used if an appropriate technical justification is included in the hardcopy monitoring plan. An alternative O<sub>2</sub> span value below 15.0 percent O<sub>2</sub> may be used if an appropriate technical justification is included in the monitoring plan (e.g., O<sub>2</sub> concentrations above a certain level create an unsafe operating condition). Select the full-scale range of the instrument to be consistent with section 2.1 of this appendix and to be greater than or equal to the span value. Select the calibration gas concentrations for the daily calibration error tests and linearity checks in accordance with section 5.1 of this appendix, as percentages of the

## **Attachment: Mercury Monitoring Provisions**

span value. For O<sub>2</sub> monitors with span values  $\geq 21.0$  percent O<sub>2</sub>, purified instrument air containing 20.9 percent O<sub>2</sub> may be used as the high-level calibration material. If a dual-range or autoranging diluent analyzer is installed, the analyzer may be represented in the monitoring plan as a single component, using a special component type code specified by the DEQ to satisfy the requirements of 40 CFR 75.53(e)(1)(iv)(D).

### **2.1.3.1 Maximum Potential Concentration of CO<sub>2</sub>**

The MPC and MEC values for diluent monitors are subject to the same periodic review as SO<sub>2</sub> and NO<sub>x</sub> monitors (see sections 2.1.1.5 and 2.1.2.5 of this appendix). If an MPC or MEC value is found to be either inappropriately high or low, the MPC shall be adjusted and corresponding span and range adjustments shall be made, if necessary.

For CO<sub>2</sub> pollutant concentration monitors, the maximum potential concentration shall be 14.0 percent CO<sub>2</sub> for boilers and 6.0 percent CO<sub>2</sub> for combustion turbines. Alternatively, the permittee may determine the MPC based on a minimum of 720 hours of quality-assured historical CEM data representing the full operating load range of the unit(s). Note that the MPC for CO<sub>2</sub> monitors shall only be used for the purpose of providing substitute data under this attachment. The CO<sub>2</sub> monitor span and range shall be determined according to section 2.1.3 of this appendix.

### **2.1.3.2 Minimum Potential Concentration of O<sub>2</sub>**

The permittee of a unit that uses a flow monitor and an O<sub>2</sub> diluent monitor to determine heat input in accordance with Equation F-17 or F-18 in appendix F to this attachment shall, for the purposes of providing substitute data under 40 CFR 75.36, determine the minimum potential O<sub>2</sub> concentration. The minimum potential O<sub>2</sub> concentration shall be based upon 720 hours or more of quality-assured CEM data, representing the full operating load range of the unit(s). The minimum potential O<sub>2</sub> concentration shall be the lowest quality-assured hourly average O<sub>2</sub> concentration recorded in the 720 (or more) hours of data used for the determination.

### **2.1.3.3 Adjustment of Span and Range**

The MPC and MEC values for diluent monitors are subject to the same periodic review as SO<sub>2</sub> and NO<sub>x</sub> monitors (see sections 2.1.1.5 and 2.1.2.5 of this appendix). If an MPC or MEC value is found to be either inappropriately high or low, the MPC shall be adjusted and corresponding span and range adjustments shall be made, if necessary. Adjust the span value and range of a CO<sub>2</sub> or O<sub>2</sub> monitor in accordance with section 2.1.1.5 of this appendix (insofar as those provisions are applicable), with the term "CO<sub>2</sub> or O<sub>2</sub>" applying instead of the term "SO<sub>2</sub>". Set the new span and range in accordance with section 2.1.3 of this appendix and report the new span value in the monitoring plan.

## Attachment: Mercury Monitoring Provisions

### 2.1.4 Flow Monitors

Select the full-scale range of the flow monitor so that it is consistent with section 2.1 of this appendix and can accurately measure all potential volumetric flow rates at the flow monitor installation site.

#### 2.1.4.1 Maximum Potential Velocity and Flow Rate

For this purpose, determine the span value of the flow monitor using the following procedure. Calculate the maximum potential velocity (MPV) using Equation A-3a or A-3b or determine the MPV (wet basis) from velocity traverse testing using EPA Reference Method 2 (or its allowable alternatives) in appendix A to 40 CFR part 60. If using test values, use the highest average velocity (determined from the EPA Method 2 traverses) measured at or near the maximum unit operating load (or, for units that do not produce electrical or thermal output, at the normal process operating conditions corresponding to the maximum stack gas flow rate). Express the MPV in units of wet standard feet per minute (fpm). For the purpose of providing substitute data during periods of missing flow rate data in accordance with 40 CFR 75.31 and 75.33 and as required elsewhere in this attachment, calculate the maximum potential stack gas flow rate (MPF) in units of standard cubic feet per hour (scfh), as the product of the MPV (in units of wet, standard fpm) times 60, times the cross-sectional area of the stack or duct (in ft<sup>2</sup>) at the flow monitor location.

$$MPV = \left( \frac{F_d H_f}{A} \right) \left( \frac{20.9}{20.9 - \%O_{2,d}} \right) \left( \frac{100}{100 - \%H_2O} \right) \quad (Eq. A-3a)$$

or

$$MPV = \left( \frac{F_c H_f}{A} \right) \left( \frac{100}{\%CO_{2,d}} \right) \left( \frac{100}{100 - \%H_2O} \right) \quad (Eq. A-3b)$$

Where:

MPV = maximum potential velocity (fpm, standard wet basis).

F<sub>d</sub> = dry-basis F factor (dscf/mmBtu) from Table 1, Appendix F to this attachment.

F<sub>c</sub> = carbon-based F factor (scf CO<sub>2</sub>/mmBtu) from Table 1, Appendix F to this attachment.

H<sub>f</sub> = maximum heat input (mmBtu/minute) for all units, combined, exhausting to the stack or duct where the flow monitor is located.

A = inside cross sectional area (ft<sup>2</sup>) of the flue at the flow monitor location.



## Attachment: Mercury Monitoring Provisions

%O<sub>2d</sub>= maximum oxygen concentration, percent dry basis, under normal operating conditions.

%CO<sub>2d</sub>= minimum carbon dioxide concentration, percent dry basis, under normal operating conditions.

%H<sub>2</sub>O = maximum percent flue gas moisture content under normal operating conditions.

### 2.1.4.2 Span Values and Range

Determine the span and range of the flow monitor as follows. Convert the MPV, as determined in section 2.1.4.1 of this appendix, to the same measurement units of flow rate that are used for daily calibration error tests (e.g., scfh, kscfh, kacfm, or differential pressure (inches of water)). Next, determine the "calibration span value" by multiplying the MPV (converted to equivalent daily calibration error units) by a factor no less than 1.00 and no greater than 1.25, and rounding up the result to at least two significant figures. For calibration span values in inches of water, retain at least two decimal places. Select appropriate reference signals for the daily calibration error tests as percentages of the calibration span value, as specified in section 2.2.2.1 of this appendix. Finally, calculate the "flow rate span value" (in scfh) as the product of the MPF, as determined in section 2.1.4.1 of this appendix, times the same factor (between 1.00 and 1.25) that was used to calculate the calibration span value. Round off the flow rate span value to the nearest 1000 scfh. Select the full-scale range of the flow monitor so that it is greater than or equal to the span value and is consistent with section 2.1 of this appendix. Include in the monitoring plan for the unit: calculations of the MPV, MPF, calibration span value, flow rate span value, and full-scale range (expressed both in scfh and, if different, in the measurement units of calibration).

### 2.1.4.3 Adjustment of Span and Range

For each CFB boiler, the permittee shall make a periodic evaluation of the MPV, MPF, span, and range values for each flow rate monitor (at a minimum, an annual evaluation is required) and shall make any necessary span and range adjustments with corresponding monitoring plan updates, as described in paragraphs (a) through (c) of this section 2.1.4.3. Span and range adjustments may be required, for example, as a result of changes in the fuel supply, changes in the stack or ductwork configuration, changes in the manner of operation of the unit, or installation or removal of emission controls. In implementing the provisions in paragraphs (a) and (b) of this section 2.1.4.3, note that flow rate data recorded during short-term, non-representative operating conditions (e.g., a trial burn of a different type of fuel) shall be excluded from consideration. The permittee shall keep the results of the most recent span and range evaluation on-site, in a format suitable for inspection. Make each required span or range adjustment no later than 45 days after the end of the quarter in which the need to adjust the span or range is identified.

(a) If the fuel supply, stack or ductwork configuration, operating parameters, or other conditions change such that the maximum potential flow rate changes significantly,

## **Attachment: Mercury Monitoring Provisions**

adjust the span and range to assure the continued accuracy of the flow monitor. A “significant” change in the MPV or MPF means that the guidelines of section 2.1 of this appendix can no longer be met, as determined by either a periodic evaluation by the permittee or from the results of an audit by the DEQ. The permittee should evaluate whether any planned changes in operation of the unit may affect the flow of the unit or stack and should plan any necessary span and range changes needed to account for these changes, so that they are made in as timely a manner as practicable to coordinate with the operational changes. Calculate the adjusted calibration span and flow rate span values using the procedures in section 2.1.4.2 of this appendix.

(b) Whenever the full-scale range is exceeded during a quarter, provided that the exceedance is not caused by a monitor out-of-control period, report 200.0 percent of the current full-scale range as the hourly flow rate for each hour of the full-scale exceedance. If the range is exceeded, make appropriate adjustments to the MPF, flow rate span, and range to prevent future full-scale exceedances. Calculate the new calibration span value by converting the new flow rate span value from units of scfh to units of daily calibration. A calibration error test must be performed and passed to validate data on the new range.

(c) Whenever changes are made to the MPV, MPF, full-scale range, or span value of the flow monitor, as described in paragraphs (a) and (b) of this section, record and report (as applicable) the new full-scale range setting, calculations of the flow rate span value, calibration span value, MPV, and MPF in an updated monitoring plan for the unit. The monitoring plan update shall be made in the quarter in which the changes become effective. Record and report the adjusted calibration span and reference values as parts of the records for the calibration error test required by appendix B to this attachment. Whenever the calibration span value is adjusted, use reference values for the calibration error test that meet the requirements of section 2.2.2.1 of this appendix, based on the most recent adjusted calibration span value. Perform a calibration error test according to section 2.1.1 of appendix B to this attachment whenever making a change to the flow monitor span or range, unless the range change also triggers a recertification under 40 CFR 75.20(b).

### **2.1.5 Minimum Potential Moisture Percentage**

Except as provided in section 2.1.6 of this appendix, the permittee of a unit that uses a continuous moisture monitoring system to correct emission rates and heat inputs from a dry basis to a wet basis (or vice-versa) shall, for the purpose of providing substitute data under 40 CFR 75.37, use a default value of 3.0 percent H<sub>2</sub>O as the minimum potential moisture percentage. Alternatively, the minimum potential moisture percentage may be based upon 720 hours or more of quality-assured CEM data, representing the full operating load range of the unit(s). If this option is chosen, the minimum potential moisture percentage shall be the lowest quality-assured hourly average H<sub>2</sub>O concentration recorded in the 720 (or more) hours of data used for the determination.

## **Attachment: Mercury Monitoring Provisions**

### **2.1.6 Maximum Potential Moisture Percentage**

When Equation 19–3, 19–4 or 19–8 in EPA Method 19 in appendix A to 40 CFR part 60 is used to determine NO<sub>x</sub> emission rate, the permittee of a unit that uses a continuous moisture monitoring system shall, for the purpose of providing substitute data under 40 CFR 75.37, determine the maximum potential moisture percentage. The maximum potential moisture percentage shall be based upon 720 hours or more of quality-assured CEM data, representing the full operating load range of the unit(s). The maximum potential moisture percentage shall be the highest quality-assured hourly average H<sub>2</sub>O concentration recorded in the 720 (or more) hours of data used for the determination. Alternatively, a default maximum potential moisture value of 15.0 percent H<sub>2</sub>O may be used.

### **2.1.7 Hg Monitors**

Determine the appropriate span and range value(s) for each Hg pollutant concentration monitor, so that all expected Hg concentrations can be determined accurately.

#### **2.1.7.1 Maximum Potential Concentration**

(a) The maximum potential concentration depends upon the type of coal combusted in the unit. For the initial MPC determination, there are three options:

(1) Use one of the following default values: 9 µgm/scm for bituminous coal; 10 µgm/scm for sub-bituminous coal; 16 µgm/scm for lignite, and 1 µgm/scm for waste coal, *i.e.*, anthracite culm or bituminous gob. If different coals are blended, use the highest MPC for any fuel in the blend; or

(2) You may base the MPC on the results of site-specific emission testing using the one of the Hg reference methods in 40 CFR 75.22, if the unit does not have add-on Hg emission controls or a flue gas desulfurization system, or if you test upstream of these control devices. A minimum of 3 test runs are required, at the normal operating load. Use the highest total Hg concentration obtained in any of the tests as the MPC; or

(3) You may base the MPC on 720 or more hours of historical CEMS data or data from a sorbent trap monitoring system, if the unit does not have add-on Hg emission controls or a flue gas desulfurization system (or if the CEMS or sorbent trap system is located upstream of these control devices) and if the Hg CEMS or sorbent trap system has been tested for relative accuracy against one of the Hg reference methods in 40 CFR 75.22 and has met a relative accuracy specification of 20.0% or less.

(b) For the purposes of missing data substitution, the fuel-specific or site-specific MPC values defined in paragraph (a) of this section apply to units using sorbent trap monitoring systems.

## **Attachment: Mercury Monitoring Provisions**

### **2.1.7.2 Maximum Expected Concentration**

For units with FGD systems that significantly reduce Hg emissions (including fluidized bed units that use limestone injection) and for units equipped with add-on Hg emission controls ( *e.g.* , carbon injection), determine the maximum expected Hg concentration (MEC) during normal, stable operation of the unit and emission controls. To calculate the MEC, substitute the MPC value from section 2.1.7.1 of this appendix into Equation A-2 in section 2.1.1.2 of this appendix. For units with add-on Hg emission controls, base the percent removal efficiency on design engineering calculations. For units with FGD systems, use the best available estimate of the Hg removal efficiency of the FGD system.

### **2.1.7.3 Span and Range Value(s)**

(a) For each Hg monitor, determine a high span value, by rounding the MPC value from section 2.1.7.1 of this appendix upward to the next highest multiple of 10  $\mu\text{gm}/\text{scm}$ .

(b) For an affected unit equipped with an FGD system or a unit with add-on Hg emission controls, if the MEC value from section 2.1.7.2 of this appendix is less than 20 percent of the high span value from paragraph (a) of this section, and if the high span value is 20  $\mu\text{gm}/\text{scm}$  or greater, define a second, low span value of 10  $\mu\text{gm}/\text{scm}$ .

(c) If only a high span value is required, set the full-scale range of the Hg analyzer to be greater than or equal to the span value.

(d) If two span values are required, you may either:

(1) Use two separate (high and low) measurement scales, setting the range of each scale to be greater than or equal to the high or low span value, as appropriate; or

(2) Quality-assure two segments of a single measurement scale.

### **2.1.7.4 Adjustment of Span and Range**

For each CFB boiler, the permittee shall make a periodic evaluation of the MPC, MEC, span, and range values for each Hg monitor (at a minimum, an annual evaluation is required) and shall make any necessary span and range adjustments, with corresponding monitoring plan updates. Span and range adjustments may be required, for example, as a result of changes in the fuel supply, changes in the manner of operation of the unit, or installation or removal of emission controls. In implementing the provisions in paragraphs (a) and (b) of this section, data recorded during short-term, non-representative process operating conditions ( *e.g.* , a trial burn of a different type of fuel) shall be excluded from consideration. The permittee shall keep the results of the most recent span and range evaluation on-site, in a format suitable for inspection. Make each required span or range adjustment no later than 45 days after the end of the quarter in which the need to adjust the span or range is identified, except that up to 90 days after the end of that quarter may be taken to implement a span adjustment if the calibration gas concentrations

## **Attachment: Mercury Monitoring Provisions**

currently being used for calibration error tests, system integrity checks, and linearity checks are unsuitable for use with the new span value and new calibration materials must be ordered.

(a) The guidelines of section 2.1 of this appendix do not apply to Hg monitoring systems.

(b) Whenever a full-scale range exceedance occurs during a quarter and is not caused by a monitor out-of-control period, proceed as follows:

(1) For monitors with a single measurement scale, report 200 percent of the full-scale range as the hourly Hg concentration until the readings come back on-scale and if appropriate, make adjustments to the MPC, span, and range to prevent future full-scale exceedances; or

(2) For units with two separate measurement scales, if the low range is exceeded, no further action is required, provided that the high range is available and is not out-of-control or out-of-service for any reason. However, if the high range is not able to provide quality assured data at the time of the low range exceedance or at any time during the continuation of the exceedance, report the MPC until the readings return to the low range or until the high range is able to provide quality assured data (unless the reason that the high-scale range is not able to provide quality assured data is because the high-scale range has been exceeded; if the high-scale range is exceeded follow the procedures in paragraph (b)(1) of this section).

(c) Whenever changes are made to the MPC, MEC, full-scale range, or span value of the Hg monitor, record and report (as applicable) the new full-scale range setting, the new MPC or MEC and calculations of the adjusted span value in an updated monitoring plan. The monitoring plan update shall be made in the quarter in which the changes become effective. In addition, record and report the adjusted span as part of the records for the daily calibration error test and linearity check specified by appendix B to this attachment. Whenever the span value is adjusted, use calibration gas concentrations that meet the requirements of section 5.1 of this appendix, based on the adjusted span value. When a span adjustment is so significant that the calibration gas concentrations currently being used for calibration error tests, system integrity checks and linearity checks are unsuitable for use with the new span value, then a diagnostic linearity or 3-level system integrity check using the new calibration gas concentrations must be performed and passed. Use the data validation procedures in 40 CFR 75.20(b)(3), beginning with the hour in which the span is changed.

### ***2.2 Design for Quality Control Testing***

#### **2.2.1 Pollutant Concentration and CO<sub>2</sub> or O<sub>2</sub> Monitors**

(a) Design and equip each pollutant concentration and CO<sub>2</sub> or O<sub>2</sub> monitor with a calibration gas injection port that allows a check of the entire measurement system when calibration gases are introduced. For extractive and dilution type monitors, all monitoring

## **Attachment: Mercury Monitoring Provisions**

components exposed to the sample gas, (e.g., sample lines, filters, scrubbers, conditioners, and as much of the probe as practicable) are included in the measurement system. For in situ type monitors, the calibration must check against the injected gas for the performance of all active electronic and optical components (e.g. transmitter, receiver, analyzer).

(b) Design and equip each pollutant concentration or CO<sub>2</sub> or O<sub>2</sub> monitor to allow daily determinations of calibration error (positive or negative) at the zero- and mid-or high-level concentrations specified in section 5.2 of this appendix.

### **2.2.2 Flow Monitors**

Design all flow monitors to meet the applicable performance specifications.

#### **2.2.2.1 Calibration Error Test**

Design and equip each flow monitor to allow for a daily calibration error test consisting of at least two reference values: Zero to 20 percent of span or an equivalent reference value ( e.g., pressure pulse or electronic signal) and 50 to 70 percent of span. Flow monitor response, both before and after any adjustment, must be capable of being recorded by the data acquisition and handling system. Design each flow monitor to allow a daily calibration error test of the entire flow monitoring system, from and including the probe tip (or equivalent) through and including the data acquisition and handling system, or the flow monitoring system from and including the transducer through and including the data acquisition and handling system.

#### **2.2.2.2 Interference Check**

(a) Design and equip each flow monitor with a means to ensure that the moisture expected to occur at the monitoring location does not interfere with the proper functioning of the flow monitoring system. Design and equip each flow monitor with a means to detect, on at least a daily basis, pluggage of each sample line and sensing port, and malfunction of each resistance temperature detector (RTD), transceiver or equivalent.

(b) Design and equip each differential pressure flow monitor to provide an automatic, periodic back purging (simultaneously on both sides of the probe) or equivalent method of sufficient force and frequency to keep the probe and lines sufficiently free of obstructions on at least a daily basis to prevent velocity sensing interference, and a means for detecting leaks in the system on at least a quarterly basis (manual check is acceptable).

(c) Design and equip each thermal flow monitor with a means to ensure on at least a daily basis that the probe remains sufficiently clean to prevent velocity sensing interference.

## Attachment: Mercury Monitoring Provisions

(d) Design and equip each ultrasonic flow monitor with a means to ensure on at least a daily basis that the transceivers remain sufficiently clean ( e.g., backpurging system) to prevent velocity sensing interference.

### 2.2.3 Mercury Monitors.

Design and equip each mercury monitor to permit the introduction of known concentrations of elemental Hg and HgCl<sub>2</sub> separately, at a point immediately preceding the sample extraction filtration system, such that the entire measurement system can be checked. If the Hg monitor does not have a converter, the HgCl<sub>2</sub> injection capability is not required.

## 3. Performance Specifications

### 3.1 Calibration Error

(a) The calibration error performance specifications in this section apply only to 7-day calibration error tests under sections 6.3.1 and 6.3.2 of this appendix and to the offline calibration demonstration described in section 2.1.1.2 of appendix B to this attachment. The calibration error limits for daily operation of the continuous monitoring systems required under this attachment are found in section 2.1.4(a) of appendix B to this attachment.

(b) The calibration error of SO<sub>2</sub> and NO<sub>x</sub> pollutant concentration monitors shall not deviate from the reference value of either the zero or upscale calibration gas by more than 2.5 percent of the span of the instrument, as calculated using Equation A-5 of this appendix. Alternatively, where the span value is less than 200 ppm, calibration error test results are also acceptable if the absolute value of the difference between the monitor response value and the reference value,  $|R-A|$ , in Equation A-5 of this appendix, is  $\leq 5$  ppm. The calibration error of CO<sub>2</sub> or O<sub>2</sub> monitors (including O<sub>2</sub> monitors used to measure CO<sub>2</sub> emissions or percent moisture) shall not deviate from the reference value of the zero or upscale calibration gas by  $>0.5$  percent O<sub>2</sub> or CO<sub>2</sub>, as calculated using the term  $|R-A|$  in the numerator of Equation A-5 of this appendix. The calibration error of flow monitors shall not exceed 3.0 percent of the calibration span value of the instrument, as calculated using Equation A-6 of this appendix. For differential pressure-type flow monitors, the calibration error test results are also acceptable if  $|R-A|$ , the absolute value of the difference between the monitor response and the reference value in Equation A-6, does not exceed 0.01 inches of water.

(c) The calibration error of a Hg concentration monitor shall not deviate from the reference value of either the zero or upscale calibration gas by more than 5.0 percent of the span value, as calculated using Equation A-5 of this appendix. Alternatively, if the span value is 10  $\mu\text{gm}/\text{scm}$ , the calibration error test results are also acceptable if the absolute value of the difference between the monitor response value and the reference value,  $|R-A|$ , in Equation A-5 of this appendix, is  $\leq 1.0 \mu\text{gm}/\text{scm}$ .

## Attachment: Mercury Monitoring Provisions

### 3.2 Linearity Check

For SO<sub>2</sub> and NO<sub>x</sub> pollutant concentration monitors, the error in linearity for each calibration gas concentration (low-, mid-, and high-levels) shall not exceed or deviate from the reference value by more than 5.0 percent (as calculated using equation A-4 of this appendix). Linearity check results are also acceptable if the absolute value of the difference between the average of the monitor response values and the average of the reference values,  $\overline{R-A}$ ; in equation A-4 of this appendix, is less than or equal to 5 ppm. For CO<sub>2</sub> or O<sub>2</sub> monitors (including O<sub>2</sub> monitors used to measure CO<sub>2</sub> emissions or percent moisture):

- (1) The error in linearity for each calibration gas concentration (low-, mid-, and high-levels) shall not exceed or deviate from the reference value by more than 5.0 percent as calculated using equation A-4 of this appendix; or
- (2) The absolute value of the difference between the average of the monitor response values and the average of the reference values,  $\overline{R-A}$ ; in equation A-4 of this appendix, shall be less than or equal to 0.5 percent CO<sub>2</sub> or O<sub>2</sub>, whichever is less restrictive.
- (3) For the linearity check and the 3-level system integrity check of an Hg monitor, which are required, respectively, under 40 CFR 75.20(c)(1)(ii) and (c)(1)(vi), the measurement error shall not exceed 10.0 percent of the reference value at any of the three gas levels. To calculate the measurement error at each level, take the absolute value of the difference between the reference value and mean CEM response, divide the result by the reference value, and then multiply by 100. Alternatively, the results at any gas level are acceptable if the absolute value of the difference between the average monitor response and the average reference value, *i.e.*,  $\overline{R-A}$ ; in Equation A-4 of this appendix, does not exceed 0.8 µg/m<sup>3</sup>. The principal and alternative performance specifications in this section also apply to the single-level system integrity check described in section 2.6 of appendix B to this attachment.

### 3.3 Relative Accuracy

#### 3.3.1 Relative Accuracy for SO<sub>2</sub> Monitors

- (a) The relative accuracy for SO<sub>2</sub> pollutant concentration monitors shall not exceed 10.0 percent except as provided in this section.
- (b) For affected units where the average of the reference method measurements of SO<sub>2</sub> concentration during the relative accuracy test audit is less than or equal to 250.0 ppm, the difference between the mean value of the monitor measurements and the reference method mean value shall not exceed ±15.0 ppm, wherever the relative accuracy specification of 10.0 percent is not achieved.

#### 3.3.2 Relative Accuracy for NO<sub>x</sub>-Diluent Continuous Emission Monitoring Systems



## **Attachment: Mercury Monitoring Provisions**

(a) The relative accuracy for NO<sub>x</sub>-diluent continuous emission monitoring systems shall not exceed 10.0 percent.

(b) For affected units where the average of the reference method measurements of NO<sub>x</sub> emission rate during the relative accuracy test audit is less than or equal to 0.200 lb/mmBtu, the difference between the mean value of the continuous emission monitoring system measurements and the reference method mean value shall not exceed  $\pm 0.020$  lb/mmBtu, wherever the relative accuracy specification of 10.0 percent is not achieved.

### **3.3.3 Relative Accuracy for CO<sub>2</sub> and O<sub>2</sub> Monitors**

The relative accuracy for CO<sub>2</sub> and O<sub>2</sub> monitors shall not exceed 10.0 percent. The relative accuracy test results are also acceptable if the difference between the mean value of the CO<sub>2</sub> or O<sub>2</sub> monitor measurements and the corresponding reference method measurement mean value, calculated using equation A-7 of this appendix, does not exceed  $\pm 1.0$  percent CO<sub>2</sub> or O<sub>2</sub>.

### **3.3.4 Relative Accuracy for Flow Monitors**

(a) The relative accuracy of flow monitors shall not exceed 10.0 percent at any load (or operating) level at which a RATA is performed (i.e., the low, mid, or high level, as defined in section 6.5.2.1 of this appendix).

(b) Where the average of the flow reference method measurements of gas velocity at a particular load (or operating) level of the relative accuracy test audit is less than or equal to 10.0 fps, the difference between the mean value of the flow monitor velocity measurements and the reference method mean value in fps at that level shall not exceed  $\pm 2.0$  fps, wherever the 10.0 percent relative accuracy specification is not achieved.

### **3.3.5 Combined SO<sub>2</sub>/Flow Monitoring System [Reserved]**

### **3.3.6 Relative Accuracy for Moisture Monitoring Systems**

The relative accuracy of a moisture monitoring system shall not exceed 10.0 percent. The relative accuracy test results are also acceptable if the difference between the mean value of the reference method measurements (in percent H<sub>2</sub>O) and the corresponding mean value of the moisture monitoring system measurements (in percent H<sub>2</sub>O), calculated using Equation A-7 of this appendix does not exceed  $\pm 1.5$  percent H<sub>2</sub>O.

### **3.3.7 Relative Accuracy for NO<sub>x</sub> Concentration Monitoring Systems**

(a) The following requirement applies only to NO<sub>x</sub> concentration monitoring systems (i.e., NO<sub>x</sub> pollutant concentration monitors) that are used to determine NO<sub>x</sub> mass emissions, where the permittee elects to monitor and report NO<sub>x</sub> mass emissions using a NO<sub>x</sub> concentration monitoring system and a flow monitoring system.

## **Attachment: Mercury Monitoring Provisions**

(b) The relative accuracy for NO<sub>x</sub> concentration monitoring systems shall not exceed 10.0 percent. Alternatively, where the average of the reference method measurements of NO<sub>x</sub> concentration during the relative accuracy test audit is less than or equal to 250.0 ppm, the difference between the mean value of the continuous emission monitoring system measurements and the reference method mean value shall not exceed  $\pm 15.0$  ppm, wherever the 10.0 percent relative accuracy specification is not achieved.

### *3.3.8 Relative Accuracy for Hg Monitoring Systems*

The relative accuracy of a Hg concentration monitoring system or a sorbent trap monitoring system shall not exceed 20.0 percent. Alternatively, where the average of the reference method measurements of Hg concentration during the relative accuracy test audit is less than 5.0  $\mu\text{gm}/\text{scm}$ , the test results are acceptable if the difference between the mean value of the monitor measurements and the reference method mean value does not exceed 1.0  $\mu\text{gm}/\text{scm}$ , in cases where the relative accuracy specification of 20.0 percent is not achieved.

### *3.4 Bias*

#### **3.4.1 SO<sub>2</sub> Pollutant Concentration Monitors, NO<sub>x</sub> Concentration Monitoring Systems and NO<sub>x</sub>-Diluent Continuous Emission Monitoring Systems**

SO<sub>2</sub> pollutant concentration monitors, NO<sub>x</sub>-diluent continuous emission monitoring systems and NO<sub>x</sub> concentration monitoring systems used to determine NO<sub>x</sub> mass emissions, as defined in 40 CFR 75.71(a)(2), shall not be biased low as determined by the test procedure in section 7.6 of this appendix. The bias specification applies to all SO<sub>2</sub> pollutant concentration monitors and to all NO<sub>x</sub> concentration monitoring systems, including those measuring an average SO<sub>2</sub> or NO<sub>x</sub> concentration of 250.0 ppm or less, and to all NO<sub>x</sub>-diluent continuous emission monitoring systems, including those measuring an average NO<sub>x</sub> emission rate of 0.200 lb/mmBtu or less.

#### **3.4.2 Flow Monitors**

Flow monitors shall not be biased low as determined by the test procedure in section 7.6 of this appendix. The bias specification applies to all flow monitors including those measuring an average gas velocity of 10.0 fps or less.

#### **3.4.3 Hg Monitoring Systems**

Mercury concentration monitoring systems and sorbent trap monitoring systems shall not be biased low as determined by the test procedure in section 7.6 of this appendix.

### *3.5 Cycle Time*

The cycle time for pollutant concentration monitors, oxygen monitors used to determine percent moisture, and any other monitoring component of a continuous emission

## **Attachment: Mercury Monitoring Provisions**

monitoring system that is required to perform a cycle time test shall not exceed 15 minutes.

### **4. Data Acquisition and Handling Systems**

Automated data acquisition and handling systems shall read and record the full range of pollutant concentrations and volumetric flow from zero through span and provide a continuous, permanent record of all measurements and required information as an ASCII flat file capable of transmission both by direct computer-to-computer electronic transfer via modem and EPA-provided software and by an IBM-compatible personal computer diskette. These systems also shall have the capability of interpreting and converting the individual output signals from an SO<sub>2</sub> pollutant concentration monitor, a flow monitor, a CO<sub>2</sub> monitor, an O<sub>2</sub> monitor, a NO<sub>x</sub> pollutant concentration monitor, a NO<sub>x</sub>-diluent CEMS, a moisture monitoring system, a Hg concentration monitoring system, and a sorbent trap monitoring system, to produce a continuous readout of pollutant emission rates or pollutant mass emissions (as applicable) in the appropriate units (e.g., lb/hr, lb/MMBtu, ounces/hr, tons/hr).

Data acquisition and handling systems shall also compute and record monitor calibration error; any bias adjustments to SO<sub>2</sub>, NO<sub>x</sub>, and Hg pollutant concentration data, flow rate data, Hg emission rate data, or NO<sub>x</sub> emission rate data; and all missing data procedure statistics specified in 40 CFR 75 subpart D.

For an excepted monitoring system under appendix D or E of this attachment, data acquisition and handling systems shall:

- (1) Read and record the full range of fuel flowrate through the upper range value;
- (2) Calculate and record intermediate values necessary to obtain emissions, such as mass fuel flowrate and heat input rate;
- (3) Calculate and record emissions in the appropriate units (e.g., lb/hr of SO<sub>2</sub>, lb/mmBtu of NO<sub>x</sub>);
- (4) Predict and record NO<sub>x</sub> emission rate using the heat input rate and the NO<sub>x</sub>/heat input correlation developed under appendix E of this attachment;
- (5) Calculate and record all missing data substitution values specified in appendix D or E of this attachment; and
- (6) Provide a continuous, permanent record of all measurements and required information as an ASCII flat file capable of transmission both by direct computer-to-computer electronic transfer via modem and DEQ-provided software and by an IBM-compatible personal computer diskette.

### **5. Calibration Gas**

## **Attachment: Mercury Monitoring Provisions**

### *5.1 Reference Gases*

For the purposes of 40 CFR part 75 and this attachment, calibration gases include the following:

#### 5.1.1 Standard Reference Materials (SRM)

These calibration gases may be obtained from the National Institute of Standards and Technology (NIST) at the following address: Quince Orchard and Cloppers Road, Gaithersburg, MD 20899-0001.

#### 5.1.2 SRM-Equivalent Compressed Gas Primary Reference Material (PRM)

Contact the Gas Metrology Team, Analytical Chemistry Division, Chemical Science and Technology Laboratory of NIST, at the address in section 5.1.1, for a list of vendors and cylinder gases.

#### 5.1.3 NIST Traceable Reference Materials

Contact the Gas Metrology Team, Analytical Chemistry Division, Chemical Science and Technology Laboratory of NIST, at the address in section 5.1.1, for a list of vendors and cylinder gases that meet the definition for a NIST Traceable Reference Material (NTRM) provided in 40 CFR 72.2.

#### 5.1.4 EPA Protocol Gases

(a) An EPA Protocol Gas is a calibration gas mixture prepared and analyzed according to Section 2 of the “EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards,” September 1997, EPA-600/R-97/121 or such revised procedure as approved by the DEQ (EPA Traceability Protocol).

(b) An EPA Protocol Gas must have a specialty gas producer-certified uncertainty (95-percent confidence interval) that must not be greater than 2.0 percent of the certified concentration (tag value) of the gas mixture. The uncertainty must be calculated using the statistical procedures (or equivalent statistical techniques) that are listed in Section 2.1.8 of the EPA Traceability Protocol.

(c) On and after January 1, 2009, a specialty gas producer advertising calibration gas certification with the EPA Traceability Protocol or distributing calibration gases as “EPA Protocol Gas” must participate in the EPA Protocol Gas Verification Program (PGVP) described in Section 2.1.10 of the EPA Traceability Protocol or it cannot use “EPA” in any form of advertising for these products, unless approved by the DEQ. A specialty gas producer not participating in the PGVP may not certify a calibration gas as an EPA Protocol Gas, unless approved by the DEQ.

## **Attachment: Mercury Monitoring Provisions**

(d) A copy of EPA-600/R-97/121 is available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA, 703-605-6585 or <http://www.ntis.gov>, and from <http://www.epa.gov/ttn/emc/news.html> or <http://www.epa.gov/appcdwww/tsb/index.html>.

### **5.1.5 Research Gas Mixtures**

Research gas mixtures must be vendor-certified to be within 2.0 percent of the concentration specified on the cylinder label (tag value), using the uncertainty calculation procedure in section 2.1.8 of the "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards," September 1997, EPA-600/R-97/121. Inquiries about the RGM program should be directed to: National Institute of Standards and Technology, Analytical Chemistry Division, Chemical Science and Technology Laboratory, B-324 Chemistry, Gaithersburg, MD 20899.

### **5.1.6 Zero Air Material**

Zero air material is defined in 40 CFR 72.2.

### **5.1.7 NIST/EPA-Approved Certified Reference Materials**

Existing certified reference materials (CRMs) that are still within their certification period may be used as calibration gas.

### **5.1.8 Gas Manufacturer's Intermediate Standards**

Gas manufacturer's intermediate standards is defined in 40 CFR 72.2.

### **5.1.9 Mercury Standards.**

For 7-day calibration error tests of Hg concentration monitors and for daily calibration error tests of Hg monitors, either NIST-traceable elemental Hg standards (as defined in 40 CFR 72.2) or a NIST-traceable source of oxidized Hg (as defined in 40 CFR 72.2) may be used. For linearity checks, NIST-traceable elemental Hg standards shall be used. For 3-level and single-point system integrity checks under 40 CFR 75.20(c)(1)(vi), sections 6.2(g) and 6.3.1 of this appendix, and sections 2.1.1, 2.2.1 and 2.6 of appendix B to this attachment, a NIST-traceable source of oxidized Hg shall be used. Alternatively, other NIST-traceable standards may be used for the required checks, subject to the approval of the DEQ. Notwithstanding these requirements, Hg calibration standards that are not NIST-traceable may be used for the tests described in this section until December 31, 2009. However, on and after January 1, 2010, only NIST-traceable calibration standards shall be used for these tests.

## **5.2 Concentrations**

Four concentration levels are required as follows.

## **Attachment: Mercury Monitoring Provisions**

### **5.2.1 Zero-level Concentration**

0.0 to 20.0 percent of span, including span for high-scale or both low- and high-scale for SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, and O<sub>2</sub> monitors, as appropriate.

### **5.2.2 Low-level Concentration**

20.0 to 30.0 percent of span, including span for high-scale or both low- and high-scale for SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, and O<sub>2</sub> monitors, as appropriate.

### **5.2.3 Mid-level Concentration**

50.0 to 60.0 percent of span, including span for high-scale or both low- and high-scale for SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, and O<sub>2</sub> monitors, as appropriate.

### **5.2.4 High-level Concentration**

80.0 to 100.0 percent of span, including span for high-scale or both low- and high-scale for SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, and O<sub>2</sub> monitors, as appropriate.

## **6. Certification Tests and Procedures**

### **6.1 General Requirements**

#### **6.1.1 Pretest Preparation**

Install the components of the continuous emission monitoring system (i.e., pollutant concentration monitors, CO<sub>2</sub> or O<sub>2</sub> monitor, and flow monitor) as specified in sections 1, 2, and 3 of this appendix, and prepare each system component and the combined system for operation in accordance with the manufacturer's written instructions. Operate the unit(s) during each period when measurements are made. Units may be tested on non-consecutive days. To the extent practicable, test the DAHS software prior to testing the monitoring hardware.

#### **6.1.2 Requirements for Air Emission Testing Bodies**

(a) On and after January 1, 2009, any Air Emission Testing Body (AETB) conducting relative accuracy test audits of CEMS and sorbent trap monitoring systems under this attachment must conform to the requirements of ASTM D7036–04 (incorporated by reference under 40 CFR 75.6). This section is not applicable to daily operation, daily calibration error checks, daily flow interference checks, quarterly linearity checks or routine maintenance of CEMS.

(b) The AETB shall provide to the affected source(s) certification that the AETB operates in conformance with, and that data submitted to the Agency has been collected in

## **Attachment: Mercury Monitoring Provisions**

accordance with, the requirements of ASTM D7036–04 (incorporated by reference under 40 CFR 75.6). This certification may be provided in the form of:

- (1) A certificate of accreditation of relevant scope issued by a recognized, national accreditation body; or
  - (2) A letter of certification signed by a member of the senior management staff of the AETB.
- (c) The AETB shall either provide a Qualified Individual on-site to conduct or shall oversee all relative accuracy testing carried out by the AETB as required in ASTM D7036–04 (incorporated by reference under 40 CFR 75.6). The Qualified Individual shall provide the affected source(s) with copies of the qualification credentials relevant to the scope of the testing conducted.

### ***6.2 Linearity Check (General Procedures)***

Check the linearity of each SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, Hg, and O<sub>2</sub> monitor while the unit, or group of units for a common stack, is combusting fuel at conditions of typical stack temperature and pressure; it is not necessary for the unit to be generating electricity during this test. Notwithstanding these requirements, if the SO<sub>2</sub> or NO<sub>x</sub> span value for a particular monitor range is  $\leq 30$  ppm, that range is exempted from the linearity check requirements of this attachment, for initial certification, recertification, and for on-going quality-assurance. For units with two measurement ranges (high and low) for a particular parameter, perform a linearity check on both the low scale (except for SO<sub>2</sub> or NO<sub>x</sub> span values  $\leq 30$  ppm) and the high scale. Note that for a NO<sub>x</sub>-diluent monitoring system with two NO<sub>x</sub> measurement ranges, if the low NO<sub>x</sub> scale has a span value  $\leq 30$  ppm and is exempt from linearity checks, this does not exempt either the diluent monitor or the high NO<sub>x</sub> scale (if the span is  $> 30$  ppm) from linearity check requirements. For on-going quality assurance of the CEMS, perform linearity checks, using the procedures in this section, on the range(s) and at the frequency specified in section 2.2.1 of appendix B to this attachment. Challenge each monitor with calibration gas, as defined in section 5.1 of this appendix, at the low-, mid-, and high-range concentrations specified in section 5.2 of this appendix. Introduce the calibration gas at the gas injection port, as specified in section 2.2.1 of this appendix. Operate each monitor at its normal operating temperature and conditions. For extractive and dilution type monitors, pass the calibration gas through all filters, scrubbers, conditioners, and other monitor components used during normal sampling and through as much of the sampling probe as is practical. For in-situ type monitors, perform calibration checking all active electronic and optical components, including the transmitter, receiver, and analyzer. Challenge the monitor three times with each reference gas (see example data sheet in Figure 1). Do not use the same gas twice in succession. To the extent practicable, the duration of each linearity test, from the hour of the first injection to the hour of the last injection, shall not exceed 24 unit operating hours. Record the monitor response from the data acquisition and handling system. For each concentration, use the average of the responses to determine the error in linearity using Equation A–4 in this appendix. Linearity checks are acceptable for monitor or

## **Attachment: Mercury Monitoring Provisions**

monitoring system certification, recertification, or quality assurance if none of the test results exceed the applicable performance specifications in section 3.2 of this appendix. The status of emission data from a CEMS prior to and during a linearity test period shall be determined as follows:

- (a) For the initial certification of a CEMS, data from the monitoring system are considered invalid until all certification tests, including the linearity test, have been successfully completed, unless the conditional data validation procedures in 40 CFR 75.20(b)(3) are used. When the procedures in 40 CFR 75.20(b)(3) are followed, the words “initial certification” apply instead of “recertification,” and complete all of the initial certification tests by the applicable deadline in 40 CFR 75.4, rather than within the time periods specified in 40 CFR 75.20(b)(3)(iv) for the individual tests.
- (b) For the routine quality assurance linearity checks required by section 2.2.1 of appendix B to this attachment, use the data validation procedures in section 2.2.3 of appendix B to this attachment.
- (c) When a linearity test is required as a diagnostic test or for recertification, use the data validation procedures in 40 CFR 75.20(b)(3).
- (d) For linearity tests of non-redundant backup monitoring systems, use the data validation procedures in 40 CFR 75.20(d)(2)(iii).
- (e) For linearity tests performed during a grace period and after the expiration of a grace period, use the data validation procedures in sections 2.2.3 and 2.2.4, respectively, of appendix B to this attachment.
- (f) For all other linearity checks, use the data validation procedures in section 2.2.3 of appendix B to this attachment.
- (g) For Hg monitors, follow the guidelines in section 2.2.3 of this appendix in addition to the applicable procedures in section 6.2 when performing the system integrity checks described in 40 CFR 75.20(c)(1)(vi) and in sections 2.1.1, 2.2.1 and 2.6 of appendix B to this attachment.
- (h) For Hg concentration monitors, if moisture is added to the calibration gas during the required linearity checks or system integrity checks, the moisture content of the calibration gas must be accounted for. Under these circumstances, the dry basis concentration of the calibration gas shall be used to calculate the linearity error or measurement error (as applicable).

### **6.3 7-Day Calibration Error Test**

#### **6.3.1 Gas Monitor 7-day Calibration Error Test**



## Attachment: Mercury Monitoring Provisions

The following monitors and ranges are exempted from the 7-day calibration error test requirements of this attachment: The SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub> and O<sub>2</sub> monitors installed on peaking units (as defined in 40 CFR 72.2); and any SO<sub>2</sub> or NO<sub>x</sub> measurement range with a span value of 50 ppm or less. In all other cases, measure the calibration error of each SO<sub>2</sub> monitor, each NO<sub>x</sub> monitor, each Hg concentration monitor, and each CO<sub>2</sub> or O<sub>2</sub> monitor while the unit is combusting fuel (but not necessarily generating electricity) once each day for 7 consecutive operating days according to the following procedures. For Hg monitors, you may perform this test using either elemental Hg standards or a NIST-traceable source of oxidized Hg. Also for Hg monitors, if moisture is added to the calibration gas, the added moisture must be accounted for and the dry-basis concentration of the calibration gas shall be used to calculate the calibration error. (In the event that unit outages occur after the commencement of the test, the 7 consecutive unit operating days need not be 7 consecutive calendar days.) Units using dual span monitors must perform the calibration error test on both high- and low-scales of the pollutant concentration monitor. The calibration error test procedures in this section and in section 6.3.2 of this appendix shall also be used to perform the daily assessments and additional calibration error tests required under sections 2.1.1 and 2.1.3 of appendix B to this attachment. Do not make manual or automatic adjustments to the monitor settings until after taking measurements at both zero and high concentration levels for that day during the 7-day test. If automatic adjustments are made following both injections, conduct the calibration error test such that the magnitude of the adjustments can be determined and recorded. Record and report test results for each day using the unadjusted concentration measured in the calibration error test prior to making any manual or automatic adjustments (i.e., resetting the calibration). The calibration error tests should be approximately 24 hours apart, (unless the 7-day test is performed over non-consecutive days). Perform calibration error tests at both the zero-level concentration and high-level concentration, as specified in section 5.2 of this appendix. Alternatively, a mid-level concentration gas (50.0 to 60.0 percent of the span value) may be used in lieu of the high-level gas, provided that the mid-level gas is more representative of the actual stack gas concentrations. In addition, repeat the procedure for SO<sub>2</sub> and NO<sub>x</sub> pollutant concentration monitors using the low-scale for units equipped with emission controls or other units with dual span monitors. Use only calibration gas, as specified in section 5.1 of this appendix. Introduce the calibration gas at the gas injection port, as specified in section 2.2.1 of this appendix. Operate each monitor in its normal sampling mode. For extractive and dilution type monitors, pass the calibration gas through all filters, scrubbers, conditioners, and other monitor components used during normal sampling and through as much of the sampling probe as is practical. For in-situ type monitors, perform calibration, checking all active electronic and optical components, including the transmitter, receiver, and analyzer. Challenge the pollutant concentration monitors and CO<sub>2</sub> or O<sub>2</sub> monitors once with each calibration gas. Record the monitor response from the data acquisition and handling system. Using Equation A-5 of this appendix, determine the calibration error at each concentration once each day (at approximately 24-hour intervals) for 7 consecutive days according to the procedures given in this section. The results of a 7-day calibration error test are acceptable for monitor or monitoring system certification, recertification or diagnostic testing if none of these daily calibration error test results exceed the applicable performance specifications in section 3.1 of this appendix. The status of emission data

## **Attachment: Mercury Monitoring Provisions**

from a gas monitor prior to and during a 7-day calibration error test period shall be determined as follows:

(a) For initial certification, data from the monitor are considered invalid until all certification tests, including the 7-day calibration error test, have been successfully completed, unless the conditional data validation procedures in 40 CFR 75.20(b)(3) are used. When the procedures in 40 CFR 75.20(b)(3) are followed, the words “initial certification” apply instead of “recertification,” and complete all of the initial certification tests by the applicable deadline in 40 CFR 75.4, rather than within the time periods specified in 40 CFR 75.20(b)(3)(iv) for the individual tests.

(b) When a 7-day calibration error test is required as a diagnostic test or for recertification, use the data validation procedures in 40 CFR 75.20(b)(3).

### **6.3.2 Flow Monitor 7-day Calibration Error Test**

Flow monitors installed on peaking units (as defined in 40 CFR 72.2) are exempted from the 7-day calibration error test requirements of this attachment. In all other cases, perform the 7-day calibration error test of a flow monitor, when required for certification, recertification or diagnostic testing, according to the following procedures. Introduce the reference signal corresponding to the values specified in section 2.2.2.1 of this appendix to the probe tip (or equivalent), or to the transducer. During the 7-day certification test period, conduct the calibration error test while the unit is operating once each unit operating day (as close to 24-hour intervals as practicable). In the event that unit outages occur after the commencement of the test, the 7 consecutive operating days need not be 7 consecutive calendar days. Record the flow monitor responses by means of the data acquisition and handling system. Calculate the calibration error using Equation A-6 of this appendix. Do not perform any corrective maintenance, repair, or replacement upon the flow monitor during the 7-day test period other than that required in the quality assurance/quality control plan required by appendix B to this attachment. Do not make adjustments between the zero and high reference level measurements on any day during the 7-day test. If the flow monitor operates within the calibration error performance specification (i.e., less than or equal to 3.0 percent error each day and requiring no corrective maintenance, repair, or replacement during the 7-day test period), the flow monitor passes the calibration error test. Record all maintenance activities and the magnitude of any adjustments. Record output readings from the data acquisition and handling system before and after all adjustments. Record and report all calibration error test results using the unadjusted flow rate measured in the calibration error test prior to resetting the calibration. Record all adjustments made during the 7-day period at the time the adjustment is made, and report them in the certification or recertification application. The status of emissions data from a flow monitor prior to and during a 7-day calibration error test period shall be determined as follows:

(a) For initial certification, data from the monitor are considered invalid until all certification tests, including the 7-day calibration error test, have been successfully completed, unless the conditional data validation procedures in 40 CFR 75.20(b)(3) are

## **Attachment: Mercury Monitoring Provisions**

used. When the procedures in 40 CFR 75.20(b)(3) are followed, the words “initial certification” apply instead of “recertification,” and complete all of the initial certification tests by the applicable deadline in 40 CFR 75.4, rather than within the time periods specified in 40 CFR 75.20(b)(3)(iv) for the individual tests.

(b) When a 7-day calibration error test is required as a diagnostic test or for recertification, use the data validation procedures in 40 CFR 75.20(b)(3).

6.3.3 For gas or flow monitors installed on peaking units, the exemption from performing the 7-day calibration error test applies as long as the unit continues to meet the definition of a peaking unit in 40 CFR 72.2. However, if at the end of a particular calendar year or ozone season, it is determined that peaking unit status has been lost, the permittee shall perform a diagnostic 7-day calibration error test of each monitor installed on the unit, by no later than December 31 of the following calendar year.

### *6.4 Cycle Time Test*

Perform cycle time tests for each pollutant concentration monitor and continuous emission monitoring system while the unit is operating, according to the following procedures. Use a zero-level and a high-level calibration gas (as defined in section 5.2 of this appendix) alternately. For Hg monitors, the calibration gas used for this test may either be the elemental or oxidized form of Hg. To determine the downscale cycle time, measure the concentration of the flue gas emissions until the response stabilizes. Record the stable emissions value. Inject a zero-level concentration calibration gas into the probe tip (or injection port leading to the calibration cell, for in situ systems with no probe). Record the time of the zero gas injection, using the data acquisition and handling system (DAHS). Next, allow the monitor to measure the concentration of the zero gas until the response stabilizes. Record the stable ending calibration gas reading. Determine the downscale cycle time as the time it takes for 95.0 percent of the step change to be achieved between the stable stack emissions value and the stable ending zero gas reading. Then repeat the procedure, starting with stable stack emissions and injecting the high-level gas, to determine the upscale cycle time, which is the time it takes for 95.0 percent of the step change to be achieved between the stable stack emissions value and the stable ending high-level gas reading. Use the following criteria to assess when a stable reading of stack emissions or calibration gas concentration has been attained. A stable value is equivalent to a reading with a change of less than 2.0 percent of the span value for 2 minutes, or a reading with a change of less than 6.0 percent from the measured average concentration over 6 minutes. Alternatively, the reading is considered stable if it changes by no more than 0.5 ppm, 0.5  $\mu\text{g}/\text{m}^3$  (for Hg), or 0.2%  $\text{CO}_2$  or  $\text{O}_2$  (as applicable) for two minutes. (Owners or operators of systems which do not record data in 1-minute or 3-minute intervals may petition the DEQ under 40 CFR 75.66 for alternative stabilization criteria). For monitors or monitoring systems that perform a series of operations (such as purge, sample, and analyze), time the injections of the calibration gases so they will produce the longest possible cycle time. Refer to Figures 6a and 6b in this appendix for example calculations of upscale and downscale cycle times. Report the slower of the two cycle times (upscale or downscale) as the cycle time for the analyzer. Prior to January 1,

## **Attachment: Mercury Monitoring Provisions**

2009 for the NO<sub>x</sub>-diluent continuous emission monitoring system test, either record and report the longer cycle time of the two component analyzers as the system cycle time or record the cycle time for each component analyzer separately (as applicable). On and after January 1, 2009, record the cycle time for each component analyzer separately. For time-shared systems, perform the cycle time tests at each probe locations that will be polled within the same 15-minute period during monitoring system operations. To determine the cycle time for time-shared systems, at each monitoring location, report the sum of the cycle time observed at that monitoring location plus the sum of the time required for all purge cycles (as determined by the continuous emission monitoring system manufacturer) at each of the probe locations of the time-shared systems. For monitors with dual ranges, report the test results for each range separately. Cycle time test results are acceptable for monitor or monitoring system certification, recertification or diagnostic testing if none of the cycle times exceed 15 minutes. The status of emissions data from a monitor prior to and during a cycle time test period shall be determined as follows:

(a) For initial certification, data from the monitor are considered invalid until all certification tests, including the cycle time test, have been successfully completed, unless the conditional data validation procedures in 40 CFR 75.20(b)(3) are used. When the procedures in 40 CFR 75.20(b)(3) are followed, the words “initial certification” apply instead of “recertification,” and complete all of the initial certification tests by the applicable deadline in 40 CFR 75.4, rather than within the time periods specified in 40 CFR 75.20(b)(3)(iv) for the individual tests.

(b) When a cycle time test is required as a diagnostic test or for recertification, use the data validation procedures in 40 CFR 75.20(b)(3).

### *6.5 Relative Accuracy and Bias Tests (General Procedures)*

Perform the required relative accuracy test audits (RATAs) as follows for each CO<sub>2</sub> emissions concentration monitor (including O<sub>2</sub> monitors used to determine CO<sub>2</sub> emissions concentration), each SO<sub>2</sub> pollutant concentration monitor, each NO<sub>x</sub> concentration monitoring system used to determine NO<sub>x</sub> mass emissions, each flow monitor, each NO<sub>x</sub>-diluent CEMS, each O<sub>2</sub> or CO<sub>2</sub> diluent monitor used to calculate heat input, each Hg concentration monitoring system, each sorbent trap monitoring system, and each moisture monitoring system. For NO<sub>x</sub> concentration monitoring systems used to determine NO<sub>x</sub> mass emissions, as defined in 40 CFR 75.71(a)(2), use the same general RATA procedures as for SO<sub>2</sub> pollutant concentration monitors; however, use the reference methods for NO<sub>x</sub> concentration specified in section 6.5.10 of this appendix:

(a) Except as otherwise provided in this paragraph or in 40 CFR 75.21(a)(5), perform each RATA while the unit (or units, if more than one unit exhausts into the flue) is combusting the fuel that is a normal primary or backup fuel for that unit (for some units, more than one type of fuel may be considered normal, e.g., a unit that combusts gas or oil on a seasonal basis). For units that co-fire fuels as the predominant mode of operation, perform the RATAs while co-firing. For Hg monitoring systems, perform the RATAs

## **Attachment: Mercury Monitoring Provisions**

while the unit is combusting coal. When relative accuracy test audits are performed on CEMS installed on bypass stacks/ducts, use the fuel normally combusted by the unit (or units, if more than one unit exhausts into the flue) when emissions exhaust through the bypass stack/ducts.

(b) Perform each RATA at the load (or operating) level(s) specified in section 6.5.1 or 6.5.2 of this appendix or in section 2.3.1.3 of appendix B to this attachment, as applicable.

(c) For monitoring systems with dual ranges, perform the relative accuracy test on the range normally used for measuring emissions. For units with add-on SO<sub>2</sub> or NO<sub>x</sub> controls or add-on Hg controls that operate continuously rather than seasonally, or for units that need a dual range to record high concentration “spikes” during startup conditions, the low range is considered normal. However, for some dual span units (e.g., for units that use fuel switching or for which the emission controls are operated seasonally), provided that both monitor ranges are connected to a common probe and sample interface, either of the two measurement ranges may be considered normal; in such cases, perform the RATA on the range that is in use at the time of the scheduled test. If the low and high measurement ranges are connected to separate sample probes and interfaces, RATA testing on both ranges is required.

(d) Record monitor or monitoring system output from the data acquisition and handling system.

(e) Complete each single-load relative accuracy test audit within a period of 168 consecutive unit operating hours, as defined in 40 CFR 72.2 (or, for CEMS installed on common stacks or bypass stacks, 168 consecutive stack operating hours, as defined in 40 CFR 72.2). Notwithstanding this requirement, up to 336 consecutive unit or stack operating hours may be taken to complete the RATA of a Hg monitoring system, when ASTM 6784–02 (incorporated by reference under 40 CFR 75.6) or EPA Method 29 in appendix A–8 to 40 CFR part 60 is used as the reference method. For 2-level and 3-level flow monitor RATAs, complete all of the RATAs at all levels, to the extent practicable, within a period of 168 consecutive unit (or stack) operating hours; however, if this is not possible, up to 720 consecutive unit (or stack) operating hours may be taken to complete a multiple-load flow RATA.

(f) The status of emission data from the CEMS prior to and during the RATA test period shall be determined as follows:

(1) For the initial certification of a CEMS, data from the monitoring system are considered invalid until all certification tests, including the RATA, have been successfully completed, unless the conditional data validation procedures in 40 CFR 75.20(b)(3) are used. When the procedures in 40 CFR 75.20(b)(3) are followed, the words “initial certification” apply instead of “recertification,” and complete all of the initial certification tests by the applicable deadline in 40 CFR 75.4, rather than within the time periods specified in 40 CFR 75.20(b)(3)(iv) for the individual tests.

## **Attachment: Mercury Monitoring Provisions**

(2) For the routine quality assurance RATAs required by section 2.3.1 of appendix B to this attachment, use the data validation procedures in section 2.3.2 of appendix B to this attachment.

(3) For recertification RATAs, use the data validation procedures in 40 CFR 75.20(b)(3).

(4) For quality assurance RATAs of non-redundant backup monitoring systems, use the data validation procedures in 40 CFR 75.20(d)(2)(v) and (vi).

(5) For RATAs performed during and after the expiration of a grace period, use the data validation procedures in sections 2.3.2 and 2.3.3, respectively, of appendix B to this attachment.

(6) For all other RATAs, use the data validation procedures in section 2.3.2 of appendix B to this attachment.

(g) For each SO<sub>2</sub> or CO<sub>2</sub> emissions concentration monitor, each flow monitor, each CO<sub>2</sub> or O<sub>2</sub> diluent monitor used to determine heat input, each NO<sub>x</sub> concentration monitoring system used to determine NO<sub>x</sub> mass emissions, as defined in 40 CFR 75.71(a)(2), each moisture monitoring system, each NO<sub>x</sub>-diluent CEMS, each Hg concentration monitoring system, and each sorbent trap monitoring system, calculate the relative accuracy, in accordance with section 7.3 or 7.4 of this appendix, as applicable. In addition (except for CO<sub>2</sub>, O<sub>2</sub>, or moisture monitors), test for bias and determine the appropriate bias adjustment factor, in accordance with sections 7.6.4 and 7.6.5 of this appendix, using the data from the relative accuracy test audits.

### **6.5.1 Gas Monitoring System RATAs (Special Considerations)**

(a) Perform the required relative accuracy test audits for each SO<sub>2</sub> or CO<sub>2</sub> emissions concentration monitor, each CO<sub>2</sub> or O<sub>2</sub> diluent monitor used to determine heat input, each NO<sub>x</sub>-diluent CEMS, each NO<sub>x</sub> concentration monitoring system used to determine NO<sub>x</sub> mass emissions, as defined in 40 CFR 75.71(a)(2), each Hg concentration monitoring system, and each sorbent trap monitoring system at the normal load level or normal operating level for the unit (or combined units, if common stack), as defined in section 6.5.2.1 of this appendix. If two load levels or operating levels have been designated as normal, the RATAs may be done at either load level.

(b) For the initial certification of a gas or Hg monitoring system and for recertifications in which, in addition to a RATA, one or more other tests are required (*i.e.*, a linearity test, cycle time test, or 7-day calibration error test), DEQ recommends that the RATA not be commenced until the other required tests of the CEMS have been passed.

### **6.5.2 Flow Monitor RATAs (Special Considerations)**

(a) Except as otherwise provided in paragraph (b) or (e) of this section, perform relative accuracy test audits for the initial certification of each flow monitor at three different

## **Attachment: Mercury Monitoring Provisions**

exhaust gas velocities (low, mid, and high), corresponding to three different load levels or operating levels within the range of operation, as defined in section 6.5.2.1 of this appendix. For a common stack/duct, the three different exhaust gas velocities may be obtained from frequently used unit/load or operating level combinations for the units exhausting to the common stack. Select the three exhaust gas velocities such that the audit points at adjacent load or operating levels (i.e., low and mid or mid and high), in megawatts (or in thousands of lb/hr of steam production or in ft/sec, as applicable), are separated by no less than 25.0 percent of the range of operation, as defined in section 6.5.2.1 of this appendix.

(b) For flow monitors on bypass stacks/ducts and peaking units, the flow monitor relative accuracy test audits for initial certification and recertification shall be single-load tests, performed at the normal load, as defined in section 6.5.2.1(d) of this appendix.

(c) Flow monitor recertification RATAs shall be done at three load level(s) (or three operating levels), unless otherwise specified in paragraph (b) or (e) of this section or unless otherwise specified or approved by the DEQ.

(d) The semiannual and annual quality assurance flow monitor RATAs required under appendix B to this attachment shall be done at the load level(s) (or operating levels) specified in section 2.3.1.3 of appendix B to this attachment.

(e) For flow monitors installed on units that do not produce electrical or thermal output, the flow RATAs for initial certification or recertification may be done at fewer than three operating levels, if:

(1) The permittee provides a technical justification in the hardcopy portion of the monitoring plan for the unit required under 40 CFR 75.53(e)(2), demonstrating that the unit operates at only one level or two levels during normal operation (excluding unit startup and shutdown). Appropriate documentation and data must be provided to support the claim of single-level or two-level operation; and

(2) The justification provided in paragraph (e)(1) of this section is deemed to be acceptable by the permitting authority.

### **6.5.2.1 Range of Operation and Normal Load (or Operating) Level(s)**

(a) The permittee shall determine the upper and lower boundaries of the “range of operation” as follows for each unit (or combination of units, for common stack configurations):

(1) For affected units that produce electrical output (in megawatts) or thermal output (in klb/hr of steam production or mmBtu/hr), the lower boundary of the range of operation of a unit shall be the minimum safe, stable loads for any of the units discharging through the stack. Alternatively, for a group of frequently-operated units that serve a common stack, the sum of the minimum safe, stable loads for the individual units may be used as the

## Attachment: Mercury Monitoring Provisions

lower boundary of the range of operation. The upper boundary of the range of operation of a unit shall be the maximum sustainable load. The "maximum sustainable load" is the higher of either: the nameplate or rated capacity of the unit, less any physical or regulatory limitations or other deratings; or the highest sustainable load, based on at least four quarters of representative historical operating data. For common stacks, the maximum sustainable load is the sum of all of the maximum sustainable loads of the individual units discharging through the stack, unless this load is unattainable in practice, in which case use the highest sustainable combined load for the units that discharge through the stack. Based on at least four quarters of representative historical operating data. The load values for the unit(s) shall be expressed either in units of megawatts or thousands of lb/hr of steam load or mmBtu/hr of thermal output; or

(2) For affected units that do not produce electrical or thermal output, the lower boundary of the range of operation shall be the minimum expected flue gas velocity (in ft/sec) during normal, stable operation of the unit. The upper boundary of the range of operation shall be the maximum potential flue gas velocity (in ft/sec) as defined in section 2.1.4.1 of this appendix. The minimum expected and maximum potential velocities may be derived from the results of reference method testing or by using Equation A-3a or A-3b (as applicable) in section 2.1.4.1 of this appendix. If Equation A-3a or A-3b is used to determine the minimum expected velocity, replace the word "maximum" with the word "minimum" in the definitions of "MPV," " $H_f$ ," " $\% O_{2d}$ ," and " $\% H_2O$ ," and replace the word "minimum" with the word "maximum" in the definition of " $CO_{2d}$ ." Alternatively, 0.0 ft/sec may be used as the lower boundary of the range of operation.

(b) The operating levels for relative accuracy test audits shall, except for peaking units, be defined as follows: the "low" operating level shall be the first 30.0 percent of the range of operation; the "mid" operating level shall be the middle portion ( $>30.0$  percent, but  $\leq 60.0$  percent) of the range of operation; and the "high" operating level shall be the upper end ( $>60.0$  percent) of the range of operation. For example, if the upper and lower boundaries of the range of operation are 100 and 1100 megawatts, respectively, then the low, mid, and high operating levels would be 100 to 400 megawatts, 400 to 700 megawatts, and 700 to 1100 megawatts, respectively.

(c) The permittee shall identify, for each CFB boiler, the "normal" load level or levels (low, mid or high), based on the operating history of the unit(s). To identify the normal load level(s), the permittee shall, at a minimum, determine the relative number of operating hours at each of the three load levels, low, mid and high over the past four representative operating quarters. The permittee shall determine, to the nearest 0.1 percent, the percentage of the time that each load level (low, mid, high) has been used during that time period. A summary of the data used for this determination and the calculated results shall be kept on-site in a format suitable for inspection. The data analysis in this paragraph may be based on fewer than four quarters of data if fewer than four representative quarters of historical load data are available. Or, if no historical load data are available, the permittee may designate the normal load based on the expected or projected manner of operating the unit. However, in either case, once four quarters of representative data become available, the historical load analysis shall be repeated.



## **Attachment: Mercury Monitoring Provisions**

### **(d) Determination of normal load (or operating level)**

(1) Based on the analysis of the historical load data described in paragraph (c) of this section, the permittee shall, for units that produce electrical or thermal output, designate the most frequently used load level as the normal load level for the unit (or combination of units, for common stacks). The permittee may also designate the second most frequently used load level as an additional normal load level for the unit or stack. For peaking units and LME units, normal load designations are unnecessary; the entire operating load range shall be considered normal. If the manner of operation of the unit changes significantly, such that the designated normal load(s) or the two most frequently used load levels change, the permittee shall repeat the historical load analysis and shall redesignate the normal load(s) and the two most frequently used load levels, as appropriate. A minimum of two representative quarters of historical load data are required to document that a change in the manner of unit operation has occurred. Update the electronic monitoring plan whenever the normal load level(s) and the two most frequently-used load levels are redesignated.

(2) For units that do not produce electrical or thermal output, the normal operating level(s) shall be determined using sound engineering judgment, based on knowledge of the unit and operating experience with the industrial process.

(e) The permittee shall report the upper and lower boundaries of the range of operation for each unit (or combination of units, for common stacks), in units of megawatts or thousands of lb/hr or mmBtu/hr of steam production or ft/sec (as applicable), in the electronic monitoring plan required under 40 CFR 75.53. Except for peaking units and LME units, the permittee shall indicate, in the electronic monitoring plan, the load level (or levels) designated as normal under this section and shall also indicate the two most frequently used load levels.

#### **6.5.2.2 Multi-Load (or Multi-Level) Flow RATA Results**

For each multi-load (or multi-level) flow RATA, calculate the flow monitor relative accuracy at each operating level. If a flow monitor relative accuracy test is failed or aborted due to a problem with the monitor on any level of a 2-level (or 3-level) relative accuracy test audit, the RATA must be repeated at that load (or operating) level. However, the entire 2-level (or 3-level) relative accuracy test audit does not have to be repeated unless the flow monitor polynomial coefficients or K-factor(s) are changed, in which case a 3-level RATA is required (or, a 2-level RATA, for units demonstrated to operate at only two levels, under section 6.5.2(e) of this appendix).

#### **6.5.3 [Reserved]**

#### **6.5.4 Calculations**

Using the data from the relative accuracy test audits, calculate relative accuracy and bias in accordance with the procedures and equations specified in section 7 of this appendix.

## **Attachment: Mercury Monitoring Provisions**

### **6.5.5 Reference Method Measurement Location**

Select a location for reference method measurements that is (1) accessible; (2) in the same proximity as the monitor or monitoring system location; and (3) meets the requirements of Performance Specification 2 in appendix B of 40 CFR part 60 for SO<sub>2</sub> and NO<sub>x</sub> continuous emission monitoring systems, Performance Specification 3 in appendix B of 40 CFR part 60 for CO<sub>2</sub> or O<sub>2</sub> monitors, or EPA Method 1 (or 1A) in appendix A of 40 CFR part 60 for volumetric flow, except as otherwise indicated in this section or as approved by the DEQ.

### **6.5.6 Reference Method Traverse Point Selection**

Select traverse points that ensure acquisition of representative samples of pollutant and diluent concentrations, moisture content, temperature, and flue gas flow rate over the flue cross section. To achieve this, the reference method traverse points shall meet the requirements of section 8.1.3 of Performance Specification 2 ("PS No. 2") in appendix B to 40 CFR part 60 (for SO<sub>2</sub>, NO<sub>x</sub>, and moisture monitoring system RATAs), Performance Specification 3 in appendix B to 40 CFR part 60 (for O<sub>2</sub> and CO<sub>2</sub> monitor RATAs), EPA Method 1 (or 1A) (for volumetric flow rate monitor RATAs), EPA Method 3 (for molecular weight), and EPA Method 4 (for moisture determination) in appendix A to 40 CFR part 60. The following alternative reference method traverse point locations are permitted for moisture and gas monitor RATAs:

(a) For moisture determinations where the moisture data are used only to determine stack gas molecular weight, a single reference method point, located at least 1.0 meter from the stack wall, may be used. For moisture monitoring system RATAs and for gas monitor RATAs in which moisture data are used to correct pollutant or diluent concentrations from a dry basis to a wet basis (or vice-versa), single-point moisture sampling may only be used if the 12-point stratification test described in section 6.5.6.1 of this appendix is performed prior to the RATA for at least one pollutant or diluent gas, and if the test is passed according to the acceptance criteria in section 6.5.6.3(b) of this appendix.

(b) For gas monitoring system RATAs, the permittee may use any of the following options:

(1) At any location (including locations where stratification is expected), use a minimum of six traverse points along a diameter, in the direction of any expected stratification. The points shall be located in accordance with EPA Method 1 in appendix A to 40 CFR part 60.

(2) At locations where section 8.1.3 of PS No. 2 allows the use of a short reference method measurement line (with three points located at 0.4, 1.2, and 2.0 meters from the stack wall), the permittee may use an alternative 3-point measurement line, locating the three points at 4.4, 14.6, and 29.6 percent of the way across the stack, in accordance with EPA Method 1 in appendix A to 40 CFR part 60.

## **Attachment: Mercury Monitoring Provisions**

(3) At locations where stratification is likely to occur (e.g., following a wet scrubber or when dissimilar gas streams are combined), the short measurement line from section 8.1.3 of PS No. 2 (or the alternative line described in paragraph (b)(2) of this section) may be used in lieu of the prescribed “long” measurement line in section 8.1.3 of PS No. 2, provided that the 12-point stratification test described in section 6.5.6.1 of this appendix is performed and passed one time at the location (according to the acceptance criteria of section 6.5.6.3(a) of this appendix) and provided that either the 12-point stratification test or the alternative (abbreviated) stratification test in section 6.5.6.2 of this appendix is performed and passed prior to each subsequent RATA at the location (according to the acceptance criteria of section 6.5.6.3(a) of this appendix).

(4) A single reference method measurement point, located no less than 1.0 meter from the stack wall and situated along one of the measurement lines used for the stratification test, may be used at any sampling location if the 12-point stratification test described in section 6.5.6.1 of this appendix is performed and passed prior to each RATA at the location (according to the acceptance criteria of section 6.5.6.3(b) of this appendix).

(5) If EPA Method 7E is used as the reference method for the RATA of a NO<sub>x</sub> CEMS installed on a combustion turbine, the reference method measurements may be made at the sampling points specified in section 6.1.2 of EPA Method 20 in appendix A to 40 CFR part 60.

(c) For Hg monitoring systems, use the same basic approach for traverse point selection that is used for the other gas monitoring system RATAs, except that the stratification test provisions in sections 8.1.3 through 8.1.3.5 of Method 30A shall apply, rather than the provisions of sections 6.5.6.1 through 6.5.6.3 of this appendix.

### **6.5.6.1 Stratification Test**

(a) With the unit(s) operating under steady-state conditions at the normal load level (or normal operating level), as defined in section 6.5.2.1 of this appendix, use a traversing gas sampling probe to measure the pollutant (SO<sub>2</sub> or NO<sub>x</sub>) and diluent (CO<sub>2</sub> or O<sub>2</sub>) concentrations at a minimum of twelve (12) points, located according to EPA Method 1 in appendix A to 40 CFR part 60.

(b) Use EPA Methods 6C, 7E, and 3A in appendix A to 40 CFR part 60 to make the measurements. Data from the reference method analyzers must be quality-assured by performing analyzer calibration error and system bias checks before the series of measurements and by conducting system bias and calibration drift checks after the measurements, in accordance with the procedures of Methods 6C, 7E, and 3A.

(c) Measure for a minimum of 2 minutes at each traverse point. To the extent practicable, complete the traverse within a 2-hour period.

## Attachment: Mercury Monitoring Provisions

(d) If the load has remained constant ( $\pm 3.0$  percent) during the traverse and if the reference method analyzers have passed all of the required quality assurance checks, proceed with the data analysis.

(e) Calculate the average  $\text{NO}_x$ ,  $\text{SO}_2$ , and  $\text{CO}_2$  (or  $\text{O}_2$ ) concentrations at each of the individual traverse points. Then, calculate the arithmetic average  $\text{NO}_x$ ,  $\text{SO}_2$ , and  $\text{CO}_2$  (or  $\text{O}_2$ ) concentrations for all traverse points.

### 6.5.6.2 Alternative (Abbreviated) Stratification Test

(a) With the unit(s) operating under steady-state conditions at normal load level (or normal operating level), as defined in section 6.5.2.1 of this appendix, use a traversing gas sampling probe to measure the pollutant ( $\text{SO}_2$  or  $\text{NO}_x$ ) and diluent ( $\text{CO}_2$  or  $\text{O}_2$ ) concentrations at three points. The points shall be located according to the specifications for the long measurement line in section 8.1.3 of PS No. 2 (i.e., locate the points 16.7 percent, 50.0 percent, and 83.3 percent of the way across the stack). Alternatively, the concentration measurements may be made at six traverse points along a diameter. The six points shall be located in accordance with EPA Method 1 in appendix A to 40 CFR part 60.

(b) Use EPA Methods 6C, 7E, and 3A in appendix A to 40 CFR part 60 to make the measurements. Data from the reference method analyzers must be quality-assured by performing analyzer calibration error and system bias checks before the series of measurements and by conducting system bias and calibration drift checks after the measurements, in accordance with the procedures of Methods 6C, 7E, and 3A.

(c) Measure for a minimum of 2 minutes at each traverse point. To the extent practicable, complete the traverse within a 1-hour period.

(d) If the load has remained constant ( $\pm 3.0$  percent) during the traverse and if the reference method analyzers have passed all of the required quality assurance checks, proceed with the data analysis.

(e) Calculate the average  $\text{NO}_x$ ,  $\text{SO}_2$ , and  $\text{CO}_2$  (or  $\text{O}_2$ ) concentrations at each of the individual traverse points. Then, calculate the arithmetic average  $\text{NO}_x$ ,  $\text{SO}_2$ , and  $\text{CO}_2$  (or  $\text{O}_2$ ) concentrations for all traverse points.

### 6.5.6.3 Stratification Test Results and Acceptance Criteria

(a) For each pollutant or diluent gas, the short reference method measurement line described in section 8.1.3 of PS No. 2 may be used in lieu of the long measurement line prescribed in section 8.1.3 of PS No. 2 if the results of a stratification test, conducted in accordance with section 6.5.6.1 or 6.5.6.2 of this appendix (as appropriate; see section 6.5.6(b)(3) of this appendix), show that the concentration at each individual traverse point differs by no more than  $\pm 10.0$  percent from the arithmetic average concentration for all traverse points. The results are also acceptable if the concentration at each individual

## Attachment: Mercury Monitoring Provisions

traverse point differs by no more than  $\pm 5$  ppm or  $\pm 0.5$  percent  $\text{CO}_2$  (or  $\text{O}_2$ ) from the arithmetic average concentration for all traverse points.

(b) For each pollutant or diluent gas, a single reference method measurement point, located at least 1.0 meter from the stack wall and situated along one of the measurement lines used for the stratification test, may be used for that pollutant or diluent gas if the results of a stratification test, conducted in accordance with section 6.5.6.1 of this appendix, show that the concentration at each individual traverse point differs by no more than  $\pm 5.0$  percent from the arithmetic average concentration for all traverse points. The results are also acceptable if the concentration at each individual traverse point differs by no more than  $\pm 3$  ppm or  $\pm 0.3$  percent  $\text{CO}_2$  (or  $\text{O}_2$ ) from the arithmetic average concentration for all traverse points.

(c) The permittee shall keep the results of all stratification tests on-site, in a format suitable for inspection, as part of the supplementary RATA records required under 40 CFR 75.59(a)(7).

### 6.5.7 Sampling Strategy

(a) Conduct the reference method tests so they will yield results representative of the pollutant concentration, emission rate, moisture, temperature, and flue gas flow rate from the unit and can be correlated with the pollutant concentration monitor,  $\text{CO}_2$  or  $\text{O}_2$  monitor, flow monitor, and  $\text{SO}_2$ , Hg, or  $\text{NO}_x$  CEMS measurements. The minimum acceptable time for a gas monitoring system RATA run or for a moisture monitoring system RATA run is 21 minutes. For each run of a gas monitoring system RATA, all necessary pollutant concentration measurements, diluent concentration measurements, and moisture measurements (if applicable) must, to the extent practicable, be made within a 60-minute period. For  $\text{NO}_x$ -diluent monitoring system RATAs, the pollutant and diluent concentration measurements must be made simultaneously. For flow monitor RATAs, the minimum time per run shall be 5 minutes. Flow rate reference method measurements may be made either sequentially from port to port or simultaneously at two or more sample ports. The velocity measurement probe may be moved from traverse point to traverse point either manually or automatically. If, during a flow RATA, significant pulsations in the reference method readings are observed, be sure to allow enough measurement time at each traverse point to obtain an accurate average reading when a manual readout method is used (e.g., a "sight-weighted" average from a manometer). Also, allow sufficient measurement time to ensure that stable temperature readings are obtained at each traverse point, particularly at the first measurement point at each sample port, when a probe is moved sequentially from port-to-port. A minimum of one set of auxiliary measurements for stack gas molecular weight determination (i.e., diluent gas data and moisture data) is required for every clock hour of a flow RATA or for every three test runs (whichever is less restrictive). Alternatively, moisture measurements for molecular weight determination may be performed before and after a series of flow RATA runs at a particular load level (low, mid, or high), provided that the time interval between the two moisture measurements does not exceed three hours. If this option is selected, the results of the two moisture determinations shall be averaged

## Attachment: Mercury Monitoring Provisions

arithmetically and applied to all RATA runs in the series. Successive flow RATA runs may be performed without waiting in-between runs. If an O<sub>2</sub>-diluent monitor is used as a CO<sub>2</sub> continuous emission monitoring system, perform a CO<sub>2</sub> system RATA (i.e., measure CO<sub>2</sub>, rather than O<sub>2</sub>, with the reference method). For moisture monitoring systems, an appropriate coefficient, “K” factor or other suitable mathematical algorithm may be developed prior to the RATA, to adjust the monitoring system readings with respect to the reference method. If such a coefficient, K-factor or algorithm is developed, it shall be applied to the CEMS readings during the RATA and (if the RATA is passed), to the subsequent CEMS data, by means of the automated data acquisition and handling system. The permittee shall keep records of the current coefficient, K factor or algorithm, as specified in 75.59(a)(5)(vii). Whenever the coefficient, K factor or algorithm is changed, a RATA of the moisture monitoring system is required. For the RATA of a Hg CEMS using the Ontario Hydro Method, or for the RATA of a sorbent trap system (irrespective of the reference method used), the time per run must be long enough to collect a sufficient mass of Hg to analyze. For the RATA of a sorbent trap monitoring system, the type of sorbent material used by the traps shall be the same as for daily operation of the monitoring system; however, the size of the traps used for the RATA may be smaller than the traps used for daily operation of the system. Spike the third section of each sorbent trap with elemental Hg, as described in section 7.1.2 of appendix K to this attachment. Install a new pair of sorbent traps prior to each test run. For each run, the sorbent trap data shall be validated according to the quality assurance criteria in section 8 of appendix K to this attachment.

(b) To properly correlate individual SO<sub>2</sub>, Hg, or NO<sub>x</sub> CEMS data (in lb/MMBtu) and volumetric flow rate data with the reference method data, annotate the beginning and end of each reference method test run (including the exact time of day) on the individual chart recorder(s) or other permanent recording device(s).

### 6.5.8 Correlation of Reference Method and Continuous Emission Monitoring System

Confirm that the monitor or monitoring system and reference method test results are on consistent moisture, pressure, temperature, and diluent concentration basis (e.g., since the flow monitor measures flow rate on a wet basis, EPA Method 2 test results must also be on a wet basis). Compare flow-monitor and reference method results on a scfh basis. Also, consider the response times of the pollutant concentration monitor, the continuous emission monitoring system, and the flow monitoring system to ensure comparison of simultaneous measurements.

For each relative accuracy test audit run, compare the measurements obtained from the monitor or continuous emission monitoring system (in ppm, percent CO<sub>2</sub>, lb/mmBtu, or other units) against the corresponding reference method values. Tabulate the paired data in a table such as the one shown in Figure 2.

### 6.5.9 Number of Reference Method Tests

## Attachment: Mercury Monitoring Provisions

Perform a minimum of nine sets of paired monitor (or monitoring system) and reference method test data for every required (i.e., certification, recertification, diagnostic, semiannual, or annual) relative accuracy test audit. For 2-level and 3-level relative accuracy test audits of flow monitors, perform a minimum of nine sets at each of the operating levels.

Note: The tester may choose to perform more than nine sets of reference method tests. If this option is chosen, the tester may reject a maximum of three sets of the test results, as long as the total number of test results used to determine the relative accuracy or bias is greater than or equal to nine. Report all data, including the rejected CEMS data and corresponding reference method test results.

### 6.5.10 Reference Methods

The following methods are from appendix A to 40 CFR part 60 or have been published by ASTM, and are the reference methods for performing relative accuracy test audits under this attachment: EPA Method 1 or 1A in appendix A-1 to 40 CFR part 60 for siting; EPA Method 2 in appendices A-1 and A-2 to 40 CFR part 60 or its allowable alternatives in appendix A to 40 CFR part 60 (except for EPA Methods 2B and 2E in appendix A-1 to 40 CFR part 60) for stack gas velocity and volumetric flow rate; EPA Methods 3, 3A or 3B in appendix A-2 to 40 CFR part 60 for O<sub>2</sub> and CO<sub>2</sub>; EPA Method 4 in appendix A-3 to 40 CFR part 60 for moisture; EPA Methods 6, 6A or 6C in appendix A-4 to 40 CFR part 60 for SO<sub>2</sub>; EPA Methods 7, 7A, 7C, 7D or 7E in appendix A-4 to 40 CFR part 60 for NO<sub>x</sub>, excluding the exceptions of EPA Method 7E in appendix A-4 to 40 CFR part 60 identified in 40 CFR 75.22(a)(5); and for Hg, either ASTM D6784-02 (the Ontario Hydro Method) (incorporated by reference under 40 CFR 75.6), EPA Method 29 in appendix A-8 to 40 CFR part 60, Method 30A, or Method 30B. When using EPA Method 7E in appendix A-4 to 40 CFR part 60 for measuring NO<sub>x</sub> concentration, total NO<sub>x</sub>, both NO and NO<sub>2</sub>, must be measured.

## 7. Calculations

### 7.1 Linearity Check

Analyze the linearity data for pollutant concentration and CO<sub>2</sub> or O<sub>2</sub> monitors as follows. Calculate the percentage error in linearity based upon the reference value at the low-level, mid-level, and high-level concentrations specified in section 6.2 of this appendix. Perform this calculation once during the certification test. Use the following equation to calculate the error in linearity for each reference value.

$$LE = \frac{|R-A|}{R} \times 100$$

(Eq. A-4)

where,

## Attachment: Mercury Monitoring Provisions

LE = Percentage Linearity error, based upon the reference value.

R = Reference value of Low-, mid-, or high-level calibration gas introduced into the monitoring system.

A = Average of the monitoring system responses.

### 7.2 Calibration Error

#### 7.2.1 Pollutant Concentration and Diluent Monitors

For each reference value, calculate the percentage calibration error based upon instrument span for daily calibration error tests using the following equation:

$$CE = \frac{|R-A|}{S} \times 100$$

(Eq. A-5)

where,

CE = Calibration error as a percentage of the span of the instrument.

R = Reference value of zero or upscale (high-level or mid-level, as applicable) calibration gas introduced into the monitoring system.

A = Actual monitoring system response to the calibration gas.

S = Span of the instrument, as specified in section 2 of this appendix.

#### 7.2.2 Flow Monitor Calibration Error

For each reference value, calculate the percentage calibration error based upon span using the following equation:

$$CE = \frac{|R-A|}{S} \times 100 \quad (\text{Eq. A-6})$$

where:

CE = Calibration error as a percentage of span.

R = Low or high level reference value specified in section 2.2.2.1 of this appendix.

A = Actual flow monitor response to the reference value.



## Attachment: Mercury Monitoring Provisions

S = Flow monitor calibration span value as determined under section 2.1.4.2 of this appendix.

### *7.3 Relative Accuracy for SO<sub>2</sub> and CO<sub>2</sub> Emissions Concentration Monitors, O<sub>2</sub> Monitors, NO<sub>x</sub> Concentration Monitoring Systems, Hg Monitoring Systems, and Flow Monitors*

Analyze the relative accuracy test audit data from the reference tests for SO<sub>2</sub> and CO<sub>2</sub> emissions concentration monitors, CO<sub>2</sub> or O<sub>2</sub> monitors used only for heat input rate determination, NO<sub>x</sub> concentration monitoring systems used to determine NO<sub>x</sub> mass emissions under 40 CFR 75 subpart H, Hg monitoring systems used to determine Hg mass emissions this attachment, and flow monitors using the following procedures. An example is shown in Figure 2. Calculate the mean of the monitor or monitoring system measurement values. Calculate the mean of the reference method values. Using data from the automated data acquisition and handling system, calculate the arithmetic differences between the reference method and monitor measurement data sets. Then calculate the arithmetic mean of the difference, the standard deviation, the confidence coefficient, and the monitor or monitoring system relative accuracy using the following procedures and equations.

#### 7.3.1 Arithmetic Mean

Calculate the arithmetic mean of the differences,  $\bar{d}$ , of a data set as follows.

$$\bar{d} = \frac{\sum_{i=1}^n d_i}{n}$$

(Eq. A-7)

where,

n = Number of data points.

n

$\sum_{i=1}^n d_i$  = Algebraic sum of the

$\sum_{i=1}^n d_i$  individual differences  $d_i$ .

$d_i$  = The difference between a reference method value and the corresponding continuous emission monitoring system value ( $RM_i - CEM_i$ ) at a given point in time  $i$ .

#### 7.3.2 Standard Deviation

Calculate the standard deviation,  $S_d$ , of a data set as follows:

## Attachment: Mercury Monitoring Provisions

$$S_d = \sqrt{\frac{\sum_{i=1}^n d_i^2 - \left[ \frac{\left( \sum_{i=1}^n d_i \right)^2}{n} \right]}{n-1}}$$

(Eq. A-8)

### 7.3.3 Confidence Coefficient

Calculate the confidence coefficient (one-tailed), cc, of a data set as follows.

$$cc = t_{0.025} \frac{S_d}{\sqrt{n}}$$

(eq. A-9)

where,

$t_{0.025}$  = t value (see table 7-1).

**Table 7-1—t-Values**

n-1	$t_{0.025}$	n-1	$t_{0.025}$	n-1	$t_{0.025}$
1	12.706	12	2.179	23	2.069
2	4.303	13	2.160	24	2.064
3	3.182	14	2.145	25	2.060
4	2.776	15	2.131	26	2.056
5	2.571	16	2.120	27	2.052
6	2.447	17	2.110	28	2.048
7	2.365	18	2.101	29	2.045
8	2.306	19	2.093	30	2.042
9	2.262	20	2.086	40	2.021
10	2.228	21	2.080	60	2.000
11	2.201	22	2.074	>60	1.960

### 7.3.4 Relative Accuracy

Calculate the relative accuracy of a data set using the following equation.

## Attachment: Mercury Monitoring Provisions

$$RA = \frac{|\bar{d}| + |cc|}{RM} \times 100$$

(Eq. A-10)

where,

RM = Arithmetic mean of the reference method values.

$\bar{d}$  = The absolute value of the mean difference between the reference method values and the corresponding continuous emission monitoring system values.

$cc$  = The absolute value of the confidence coefficient.

### 7.4 Relative Accuracy for NO<sub>x</sub>-diluent Continuous Emission Monitoring Systems

Analyze the relative accuracy test audit data from the reference method tests for NO<sub>x</sub>-diluent continuous emissions monitoring system as follows.

#### 7.4.1 Data Preparation

If C<sub>NO<sub>x</sub></sub>, the NO<sub>x</sub> concentration, is in ppm, multiply it by 1.194 × 10<sup>-7</sup>(lb/dscf)/ppm to convert it to units of lb/dscf. If C<sub>NO<sub>x</sub></sub> is in mg/dscm, multiply it by 6.24 × 10<sup>-8</sup>(lb/dscf)/(mg/dscm) to convert it to lb/dscf. Then, use the diluent (O<sub>2</sub> or CO<sub>2</sub>) reference method results for the run and the appropriate F or F<sub>c</sub> factor from table 1 in appendix F of this attachment to convert C<sub>NO<sub>x</sub></sub> from lb/dscf to lb/mmBtu units. Use the equations and procedure in section 3 of appendix F to this attachment, as appropriate.

#### 7.4.2 NO<sub>x</sub> Emission Rate

For each test run in a data set, calculate the average NO<sub>x</sub> emission rate (in lb/mmBtu), by means of the data acquisition and handling system, during the time period of the test run. Tabulate the results as shown in example Figure 4.

#### 7.4.3 Relative Accuracy

Use the equations and procedures in section 7.3 above to calculate the relative accuracy for the NO<sub>x</sub> continuous emission monitoring system. In using equation A-7, “d” is, for each run, the difference between the NO<sub>x</sub> emission rate values (in lb/mmBtu) obtained from the reference method data and the NO<sub>x</sub> continuous emission monitoring system.

### 7.5 Relative Accuracy for Combined SO<sub>2</sub>/Flow [Reserved]

### 7.6 Bias Test and Adjustment Factor

## Attachment: Mercury Monitoring Provisions

Test the following relative accuracy test audit data sets for bias: SO<sub>2</sub> pollutant concentration monitors; flow monitors; NO<sub>x</sub> concentration monitoring systems used to determine NO<sub>x</sub> mass emissions, as defined in 40 CFR 75.71(a)(2); NO<sub>x</sub>-diluent CEMS, Hg concentration monitoring systems, and sorbent trap monitoring systems, using the procedures outlined in sections 7.6.1 through 7.6.5 of this appendix. For multiple-load flow RATAs, perform a bias test at each load level designated as normal under section 6.5.2.1 of this appendix.

### 7.6.1 Arithmetic Mean

Calculate the arithmetic mean of the difference,  $d$ , of the data set using equation A-7 of this appendix. To calculate bias for an SO<sub>2</sub> or NO<sub>x</sub> pollutant concentration monitor, " $d$ " is, for each paired data point, the difference between the SO<sub>2</sub> or NO<sub>x</sub> concentration value (in ppm) obtained from the reference method and the monitor. To calculate bias for a flow monitor, " $d$ " is, for each paired data point, the difference between the flow rate values (in scfh) obtained from the reference method and the monitor. To calculate bias for a NO<sub>x</sub>-diluent continuous emission monitoring system, " $d$ " is, for each paired data point, the difference between the NO<sub>x</sub>-diluent emission rate values (in lb/mmBtu) obtained from the reference method and the monitoring system. To calculate bias for a Hg monitoring system when using the Ontario Hydro Method or EPA Method 29 in appendix A-8 to 40 CFR part 60, " $d$ " is, for each data point, the difference between the average Hg concentration value (in  $\mu\text{g}/\text{m}^3$ ) from the paired Ontario Hydro or EPA Method 29 in appendix A-8 to 40 CFR part 60 sampling trains and the concentration measured by the monitoring system. For sorbent trap monitoring systems, use the average Hg concentration measured by the paired traps in the calculation of " $d$ ".

### 7.6.2 Standard Deviation

Calculate the standard deviation,  $S_d$ , of the data set using equation A-8.

### 7.6.3 Confidence Coefficient

Calculate the confidence coefficient,  $cc$ , of the data set using equation A-9.

### 7.6.4 Bias Test

If, for the relative accuracy test audit data set being tested, the mean difference,  $d$ , is less than or equal to the absolute value of the confidence coefficient,  $\overline{cc}$ , the monitor or monitoring system has passed the bias test. If the mean difference,  $d$ , is greater than the absolute value of the confidence coefficient,  $\sqrt{cc}$ , the monitor or monitoring system has failed to meet the bias test requirement.

### 7.6.5 Bias Adjustment

(a) If the monitor or monitoring system fails to meet the bias test requirement, adjust the value obtained from the monitor using the following equation:

## Attachment: Mercury Monitoring Provisions

$$CEM_i^{Adjusted} = CEM_i^{Monitor} \times BAF \quad (Eq. A-11)$$

Where:

$CEM_i^{Monitor}$  = Data (measurement) provided by the monitor at time i.

$CEM_i^{Adjusted}$  = Data value, adjusted for bias, at time i.

BAF = Bias adjustment factor, defined by:

$$BAF = 1 + \frac{|d|}{CEM_{avg}} \quad (Eq. A-12)$$

Where:

BAF = Bias adjustment factor, calculated to the nearest thousandth.

d = Arithmetic mean of the difference obtained during the failed bias test using Equation A-7.

$CEM_{avg}$  = Mean of the data values provided by the monitor during the failed bias test.

(b) For single-load RATAs of SO<sub>2</sub> pollutant concentration monitors, NO<sub>x</sub> concentration monitoring systems, NO<sub>x</sub>-diluent monitoring systems, Hg concentration monitoring systems, and sorbent trap monitoring systems, and for the single-load flow RATAs required or allowed under section 6.5.2 of this appendix and sections 2.3.1.3(b) and 2.3.1.3(c) of appendix B to this attachment, the appropriate BAF is determined directly from the RATA results at normal load, using Equation A-12. Notwithstanding, when a NO<sub>x</sub> concentration CEMS or an SO<sub>2</sub>CEMS or a NO<sub>x</sub>-diluent CEMS installed on a low-emitting affected unit (i.e., average SO<sub>2</sub> or NO<sub>x</sub> concentration during the RATA ≤ 250 ppm or average NO<sub>x</sub> emission rate ≤ 0.200 lb/mmBtu) meets the normal 10.0 percent relative accuracy specification (as calculated using Equation A-10) or the alternate relative accuracy specification in section 3.3 of this appendix for low-emitters, but fails the bias test, the BAF may either be determined using Equation A-12, or a default BAF of 1.111 may be used. Similarly, for Hg concentration and sorbent trap monitoring systems, where the average Hg concentration during the RATA is < 5.0 µgm/dscm, if the monitoring system meets the normal or the alternative relative accuracy specification in section 3.3.8 of this appendix but fails the bias test, the permittee may either use the bias adjustment factor (BAF) calculated from Equation A-12 or may use a default BAF of 1.250 for reporting purposes under this attachment.

(c) For 2-load or 3-load flow RATAs, when only one load level (low, mid or high) has been designated as normal under section 6.5.2.1 of this appendix and the bias test is passed at the normal load level, apply a BAF of 1.000 to the subsequent flow rate data. If the bias test is failed at the normal load level, use Equation A-12 to calculate the normal

## Attachment: Mercury Monitoring Provisions

load BAF and then perform an additional bias test at the second most frequently-used load level, as determined under section 6.5.2.1 of this appendix. If the bias test is passed at this second load level, apply the normal load BAF to the subsequent flow rate data. If the bias test is failed at this second load level, use Equation A-12 to calculate the BAF at the second load level and apply the higher of the two BAFs (either from the normal load level or from the second load level) to the subsequent flow rate data.

(d) For 2-load or 3-load flow RATAs, when two load levels have been designated as normal under section 6.5.2.1 of this appendix and the bias test is passed at both normal load levels, apply a BAF of 1.000 to the subsequent flow rate data. If the bias test is failed at one of the normal load levels but not at the other, use Equation A-12 to calculate the BAF for the normal load level at which the bias test was failed and apply that BAF to the subsequent flow rate data. If the bias test is failed at both designated normal load levels, use Equation A-12 to calculate the BAF at each normal load level and apply the higher of the two BAFs to the subsequent flow rate data.

(e) Each time a RATA is passed and the appropriate bias adjustment factor has been determined, apply the BAF prospectively to all monitoring system data, beginning with the first clock hour following the hour in which the RATA was completed. For a 2-load flow RATA, the “hour in which the RATA was completed” refers to the hour in which the testing at both loads was completed; for a 3-load RATA, it refers to the hour in which the testing at all three loads was completed.

(f) Use the bias-adjusted values in computing substitution values in the missing data procedure, as specified in 40 CFR 75 subpart D, and in reporting the concentration of SO<sub>2</sub> or Hg, the flow rate, the average NO<sub>x</sub> emission rate, the unit heat input, and the calculated mass emissions of SO<sub>2</sub> and CO<sub>2</sub> during the quarter and calendar year, as specified in 40 CFR 75 subpart G. In addition, when using a NO<sub>x</sub> concentration monitoring system and a flow monitor to calculate NO<sub>x</sub> mass emissions under 40 CFR 75 subpart H, or when using a Hg concentration or sorbent trap monitoring system and a flow monitor to calculate Hg mass emissions under this attachment, use bias-adjusted values for NO<sub>x</sub> (or Hg) concentration and flow rate in the mass emission calculations and use bias-adjusted NO<sub>x</sub> (or Hg) concentrations to compute the appropriate substitution values for NO<sub>x</sub> (or Hg) concentration in the missing data routines under 40 CFR 75 subpart D.

(g) For units that do not produce electrical or thermal output, the provisions of paragraphs (a) through (f) of this section apply, except that the terms, “single-load”, “2-load”, “3-load”, and “load level” shall be replaced, respectively, with the terms, “single-level”, “2-level”, “3-level”, and “operating level”.

### 7.7 Reference Flow-to-Load Ratio or Gross Heat Rate

(a) Except as provided in section 7.8 of this appendix, the permittee shall determine  $R_{ref}$ , the reference value of the ratio of flow rate to unit load, each time that a passing flow RATA is performed at a load level designated as normal in section 6.5.2.1 of this

## Attachment: Mercury Monitoring Provisions

appendix. The permittee shall report the current value of  $R_{ref}$  in the electronic quarterly report required under 40 CFR 75.64 and shall also report the completion date of the associated RATA. If two load levels have been designated as normal under section 6.5.2.1 of this appendix, the permittee shall determine a separate  $R_{ref}$  value for each of the normal load levels. The reference flow-to-load ratio shall be calculated as follows:

$$R_{ref} = \frac{Q_{ref}}{L_{avg}} \times 10^{-5} \quad (Eq. A-13)$$

Where:

$R_{ref}$  = Reference value of the flow-to-load ratio, from the most recent normal-load flow RATA, scfh/megawatts, scfh/1000 lb/hr of steam, or scfh/(mmBtu/hr of steam output).

$Q_{ref}$  = Average stack gas volumetric flow rate measured by the reference method during the normal-load RATA, scfh.

$L_{avg}$  = Average unit load during the normal-load flow RATA, megawatts, 1000 lb/hr of steam, or mmBtu/hr of thermal output.

(b) In Equation A-13, for a common stack, determine  $L_{avg}$  by summing, for each RATA run, the operating loads of all units discharging through the common stack, and then taking the arithmetic average of the summed loads. For a unit that discharges its emissions through multiple stacks, either determine a single value of  $Q_{ref}$  for the unit or a separate value of  $Q_{ref}$  for each stack. In the former case, calculate  $Q_{ref}$  by summing, for each RATA run, the volumetric flow rates through the individual stacks and then taking the arithmetic average of the summed RATA run flow rates. In the latter case, calculate the value of  $Q_{ref}$  for each stack by taking the arithmetic average, for all RATA runs, of the flow rates through the stack. For a unit with a multiple stack discharge configuration consisting of a main stack and a bypass stack (e.g., a unit with a wet SO<sub>2</sub> scrubber), determine  $Q_{ref}$  separately for each stack at the time of the normal load flow RATA. Round off the value of  $R_{ref}$  to two decimal places.

(c) In addition to determining  $R_{ref}$  or as an alternative to determining  $R_{ref}$ , a reference value of the gross heat rate (GHR) may be determined. In order to use this option, quality-assured diluent gas (CO<sub>2</sub> or O<sub>2</sub>) must be available for each hour of the most recent normal-load flow RATA. The reference value of the GHR shall be determined as follows:

$$(GHR)_{ref} = \frac{(Heat\ Input)_{avg}}{L_{avg}} \times 1000 \quad (Eq. A-13a)$$

Where:

$(GHR)_{ref}$  = Reference value of the gross heat rate at the time of the most recent normal-load flow RATA, Btu/kwh, Btu/lb steam load, or Btu heat input/mmBtu steam output.

## Attachment: Mercury Monitoring Provisions

(Heat Input)<sub>avg</sub> = Average hourly heat input during the normal-load flow RATA, as determined using the applicable equation in appendix F to this attachment, mmBtu/hr. For multiple stack configurations, if the reference GHR value is determined separately for each stack, use the hourly heat input measured at each stack. If the reference GHR is determined at the unit level, sum the hourly heat inputs measured at the individual stacks.

L<sub>avg</sub> = Average unit load during the normal-load flow RATA, megawatts, 1000 lb/hr of steam, or mmBtu/hr thermal output.

(d) In the calculation of (Heat Input)<sub>avg</sub>, use Q<sub>ref</sub>, the average volumetric flow rate measured by the reference method during the RATA, and use the average diluent gas concentration measured during the flow RATA (i.e., the arithmetic average of the diluent gas concentrations for all clock hours in which a RATA run was performed).

### 7.8 Flow-to-Load Test Exemptions

(a) For complex stack configurations (e.g., when the effluent from a unit is divided and discharges through multiple stacks in such a manner that the flow rate in the individual stacks cannot be correlated with unit load), the permittee may petition the DEQ under 40 CFR 75.66 for an exemption from the requirements of section 7.7 of this appendix and section 2.2.5 of appendix B to this attachment. The petition must include sufficient information and data to demonstrate that a flow-to-load or gross heat rate evaluation is infeasible for the complex stack configuration.

(b) Units that do not produce electrical output (in megawatts) or thermal output (in klb of steam per hour) are exempted from the flow-to-load ratio test requirements of section 7.7 of this appendix and section 2.2.5 of appendix B to this attachment.

Figure 1 to Appendix A—Linearity Error Determination

Day	Date and time	Reference value	Monitor value	Difference	Percent of reference value
Low-level:					
Mid-					



**Attachment: Mercury Monitoring Provisions**

Day	Date and time	Reference value	Monitor value	Difference	Percent of reference value
level:					
High-level:					

**Figure 2 to Appendix A—Relative Accuracy Determination (Pollutant Concentration Monitors)**

Run No.	Date and time	SO <sub>2</sub> (ppm <sup>c</sup> )			Date and time	CO <sub>2</sub> (Pollutant) (ppm <sup>c</sup> )		
		RM <sup>a</sup>	M <sup>b</sup>	Diff		RM <sup>a</sup>	M <sup>b</sup>	Diff
1								
2								
3								
4								
5								
6								
7								

# Attachment: Mercury Monitoring Provisions

8								
9								
10								
11								
12								
Arithmetic Mean Difference (Eq. A-7). Confidence Coefficient (Eq. A-9). Relative Accuracy (Eq. A-10).								

<sup>a</sup>RM means “reference method data.”

<sup>b</sup>M means “monitor data.”

<sup>c</sup>Make sure the RM and M data are on a consistent basis, either wet or dry.

**Figure 3 to Appendix A—Relative Accuracy Determination (Flow Monitors)**

Run No.	Date and time	Flow rate (Low) (scf/hr)*			Date and time	Flow rate (Normal) (scf/hr)*			Date and time	Flow rate (High) (scf/hr)*		
		RM	M	Diff		RM	M	Diff		RM	M	Diff
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12												

### Attachment: Mercury Monitoring Provisions

Arithmetic Mean Difference (Eq. A-7). Confidence Coefficient (Eq. A-9). Relative Accuracy (Eq. A-10).														

\*Make sure the RM and M data are on a consistent basis, either wet or dry.

**Figure 4 to Appendix A—Relative Accuracy Determination (NO<sub>x</sub>/Diluent Combined System)**

Run No.	Date and time	Reference method data		NO <sub>x</sub> system (lb/mmBtu)		
		NO <sub>x</sub> ( ) <sup>a</sup>	O <sub>2</sub> /CO <sub>2</sub> %	RM	M	Difference
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
Arithmetic Mean Difference (Eq. A-7). Confidence Coefficient (Eq. A-9). Relative Accuracy (Eq. A-10).						

<sup>a</sup>Specify units: ppm, lb/dscf, mg/dscm.

### Figure 5—Cycle Time

Date of test \_\_\_\_\_  
Component/system ID#: \_\_\_\_\_

**Attachment: Mercury Monitoring Provisions**

Analyzer type \_\_\_\_\_

Serial Number \_\_\_\_\_

High level gas concentration: \_\_\_\_ ppm/% (circle one)

Zero level gas concentration: \_\_\_\_ ppm/% (circle one)

Analyzer span setting: \_\_\_\_ ppm/% (circle one)

Upscale:

Stable starting monitor value: \_\_\_\_ ppm/% (circle one)

Stable ending monitor reading: \_\_\_\_ ppm/% (circle one)

Elapsed time: \_\_\_\_ seconds

Downscale:

Stable starting monitor value: \_\_\_\_ ppm/% (circle one)

Stable ending monitor value: \_\_\_\_ ppm/% (circle one)

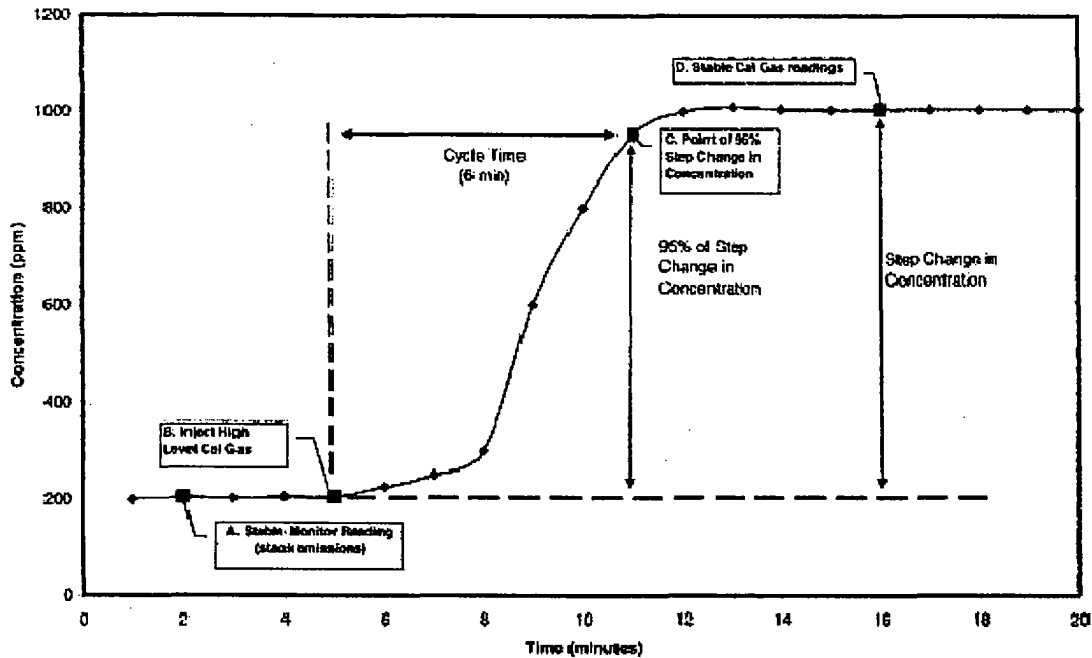
Elapsed time: \_\_\_\_ seconds

Component cycle time= \_\_\_\_ seconds

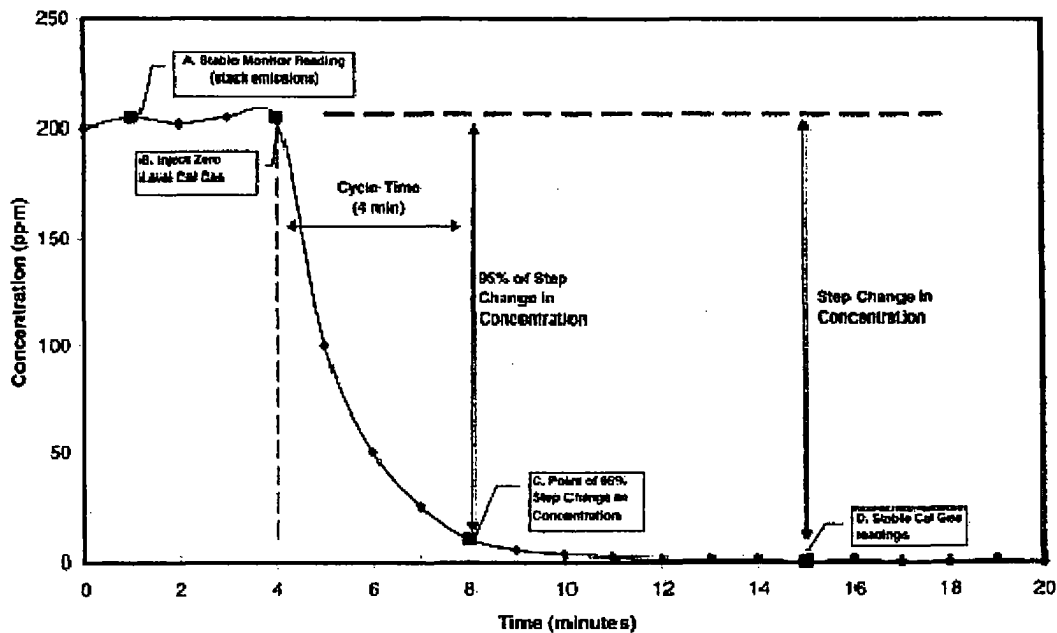
System cycle time= \_\_\_\_ seconds

## Attachment: Mercury Monitoring Provisions

**Figure 6a. Upscale Cycle Time Test**



**Figure 6b. Downscale Cycle Time Test**



A. To determine the upscale cycle time (Figure 6a), measure the flue gas emissions until the response stabilizes. Record the stabilized value (see section 6.4 of this appendix for the stability criteria).

B. Inject a high-level calibration gas into the port leading to the calibration cell or thimble (Point B). Allow the analyzer to stabilize. Record the stabilized value.

## **Attachment: Mercury Monitoring Provisions**

C. Determine the step change. The step change is equal to the difference between the final stable calibration gas value (Point D) and the stabilized stack emissions value (Point A).

D. Take 95% of the step change value and add the result to the stabilized stack emissions value (Point A). Determine the time at which 95% of the step change occurred (Point C).

E. Calculate the upscale cycle time by subtracting the time at which the calibration gas was injected (Point B) from the time at which 95% of the step change occurred (Point C). In this example, upscale cycle time =  $(11 - 5) = 6$  minutes.

F. To determine the downscale cycle time (Figure 6b) repeat the procedures above, except that a zero gas is injected when the flue gas emissions have stabilized, and 95% of the step change in concentration is subtracted from the stabilized stack emissions value.

G. Compare the upscale and downscale cycle time values. The longer of these two times is the cycle time for the analyzer.

## **Attachment: Mercury Monitoring Provisions**

### **Appendix B to Attachment —Quality Assurance and Quality Control Procedures**

#### **1. Quality Assurance/Quality Control Program**

Develop and implement a quality assurance/quality control (QA/QC) program for the continuous emission monitoring systems, excepted monitoring systems approved under appendix D or E to this attachment, and alternative monitoring systems under 40 CFR 75 subpart E, and their components. At a minimum, include in each QA/QC program a written plan that describes in detail (or that refers to separate documents containing) complete, step-by-step procedures and operations for each of the following activities. Upon request from regulatory authorities, the source shall make all procedures, maintenance records, and ancillary supporting documentation from the manufacturer (e.g., software coefficients and troubleshooting diagrams) available for review during an audit. Electronic storage of the information in the QA/QC plan is permissible, provided that the information can be made available in hardcopy upon request during an audit.

##### *1.1 Requirements for All Monitoring Systems*

###### **1.1.1 Preventive Maintenance**

Keep a written record of procedures needed to maintain the monitoring system in proper operating condition and a schedule for those procedures. This shall, at a minimum, include procedures specified by the manufacturers of the equipment and, if applicable, additional or alternate procedures developed for the equipment.

###### **1.1.2 Recordkeeping and Reporting**

Keep a written record describing procedures that will be used to implement the recordkeeping and reporting requirements in 40 CFR 75 subparts E, F, and G and appendices D and E to this attachment, as applicable.

###### **1.1.3 Maintenance Records**

Keep a record of all testing, maintenance, or repair activities performed on any monitoring system or component in a location and format suitable for inspection. A maintenance log may be used for this purpose. The following records should be maintained: date, time, and description of any testing, adjustment, repair, replacement, or preventive maintenance action performed on any monitoring system and records of any corrective actions associated with a monitor's outage period. Additionally, any adjustment that recharacterizes a system's ability to record and report emissions data must be recorded (e.g., changing of flow monitor or moisture monitoring system polynomial coefficients, K factors or mathematical algorithms, changing of temperature and pressure coefficients and dilution ratio settings), and a written explanation of the procedures used to make the adjustment(s) shall be kept.

## **Attachment: Mercury Monitoring Provisions**

1.1.4 The requirements in section 6.1.2 of appendix A to this attachment shall be met by any Air Emissions Testing Body (AETB) performing the semiannual/annual RATAs described in section 2.3 of this appendix and the Hg emission tests described in 40 CFR 75.81(c) and 75.81(d)(4).

### *1.2 Specific Requirements for Continuous Emissions Monitoring Systems*

#### 1.2.1 Calibration Error Test and Linearity Check Procedures

Keep a written record of the procedures used for daily calibration error tests and linearity checks (e.g., how gases are to be injected, adjustments of flow rates and pressure, introduction of reference values, length of time for injection of calibration gases, steps for obtaining calibration error or error in linearity, determination of interferences, and when calibration adjustments should be made). Identify any calibration error test and linearity check procedures specific to the continuous emission monitoring system that vary from the procedures in appendix A to this attachment.

#### 1.2.2 Calibration and Linearity Adjustments

Explain how each component of the continuous emission monitoring system will be adjusted to provide correct responses to calibration gases, reference values, and/or indications of interference both initially and after repairs or corrective action. Identify equations, conversion factors and other factors affecting calibration of each continuous emission monitoring system.

#### 1.2.3 Relative Accuracy Test Audit Procedures

Keep a written record of procedures and details peculiar to the installed continuous emission monitoring systems that are to be used for relative accuracy test audits, such as sampling and analysis methods.

#### 1.2.4 Parametric Monitoring for Units With Add-on Emission Controls

The permittee shall keep a written (or electronic) record including a list of operating parameters for the add-on SO<sub>2</sub> or NO<sub>x</sub> emission controls, including parameters in 40 CFR 75.55(b) or 40 CFR 75.58(b), as applicable, and the range of each operating parameter that indicates the add-on emission controls are operating properly. The permittee shall keep a written (or electronic) record of the parametric monitoring data during each SO<sub>2</sub> or NO<sub>x</sub> missing data period.

### *1.3 Specific Requirements for Excepted Systems Approved Under Appendices D and E*

#### 1.3.1 Fuel Flowmeter Accuracy Test Procedures

Keep a written record of the specific fuel flowmeter accuracy test procedures. These may include: standard methods or specifications listed in and of appendix D to this attachment



## **Attachment: Mercury Monitoring Provisions**

and incorporated by reference under 40 CFR 75.6; the procedures of sections 2.1.5.2 or 2.1.7 of appendix D to this attachment; or other methods approved by the DEQ through the petition process of 40 CFR 75.66(c).

### **1.3.2 Transducer or Transmitter Accuracy Test Procedures**

Keep a written record of the procedures for testing the accuracy of transducers or transmitters of an orifice-, nozzle-, or venturi-type fuel flowmeter under section 2.1.6 of appendix D to this attachment. These procedures should include a description of equipment used, steps in testing, and frequency of testing.

### **1.3.3 Fuel Flowmeter, Transducer, or Transmitter Calibration and Maintenance Records**

Keep a record of adjustments, maintenance, or repairs performed on the fuel flowmeter monitoring system. Keep records of the data and results for fuel flowmeter accuracy tests and transducer accuracy tests, consistent with appendix D to this attachment.

### **1.3.4 Primary Element Inspection Procedures**

Keep a written record of the standard operating procedures for inspection of the primary element (i.e., orifice, venturi, or nozzle) of an orifice-, venturi-, or nozzle-type fuel flowmeter. Examples of the types of information to be included are: what to examine on the primary element; how to identify if there is corrosion sufficient to affect the accuracy of the primary element; and what inspection tools (e.g., baroscope), if any, are used.

### **1.3.5 Fuel Sampling Method and Sample Retention**

Keep a written record of the standard procedures used to perform fuel sampling, either by utility personnel or by fuel supply company personnel. These procedures should specify the portion of the ASTM method used, as incorporated by reference under 40 CFR 75.6, or other methods approved by the DEQ through the petition process of 40 CFR 75.66(c). These procedures should describe safeguards for ensuring the availability of an oil sample (e.g., procedure and location for splitting samples, procedure for maintaining sample splits on site, and procedure for transmitting samples to an analytical laboratory). These procedures should identify the ASTM analytical methods used to analyze sulfur content, gross calorific value, and density, as incorporated by reference under 40 CFR 75.6, or other methods approved by the DEQ through the petition process of 40 CFR 75.66(c).

## ***1.4 Requirements for Alternative Systems Approved Under 40 CFR 75 Subpart E***

### **1.4.1 Daily Quality Assurance Tests**

Explain how the daily assessment procedures specific to the alternative monitoring system are to be performed.

## **Attachment: Mercury Monitoring Provisions**

### **1.4.2 Daily Quality Assurance Test Adjustments**

Explain how each component of the alternative monitoring system will be adjusted in response to the results of the daily assessments.

### **1.4.3 Relative Accuracy Test Audit Procedures**

Keep a written record of procedures and details peculiar to the installed alternative monitoring system that are to be used for relative accuracy test audits, such as sampling and analysis methods.

## ***1.5 Requirements for Sorbent Trap Monitoring Systems***

### **1.5.1 Sorbent Trap Identification and Tracking**

Include procedures for inscribing or otherwise permanently marking a unique identification number on each sorbent trap, for tracking purposes. Keep records of the ID of the monitoring system in which each sorbent trap is used, and the dates and hours of each Hg collection period.

### ***1.5.2 Monitoring System Integrity and Data Quality***

Explain the procedures used to perform the leak checks when sorbent traps are placed in service and removed from service. Also explain the other QA procedures used to ensure system integrity and data quality, including, but not limited to, gas flow meter calibrations, verification of moisture removal, and ensuring air-tight pump operation. In addition, the QA plan must include the data acceptance and quality control criteria in section 8 of appendix K to this attachment. All reference meters used to calibrate the gas flow meters (e.g., wet test meters) shall be periodically recalibrated. Annual, or more frequent, recalibration is recommended. If a NIST–traceable calibration device is used as a reference flow meter, the QA plan must include a protocol for ongoing maintenance and periodic recalibration to maintain the accuracy and NIST–traceability of the calibrator.

### **1.5.3 Hg Analysis**

Explain the chain of custody employed in packing, transporting, and analyzing the sorbent traps (see sections 7.2.8 and 7.2.9 in appendix K to this attachment). Keep records of all Hg analyses. The analyses shall be performed in accordance with the procedures described in section 10 of appendix K to this attachment.

### **1.5.4 Laboratory Certification**

The QA Plan shall include documentation that the laboratory performing the analyses on the carbon sorbent traps is certified by the International Organization for Standardization (ISO) to have a proficiency that meets the requirements of ISO 17025. Alternatively, if

## **Attachment: Mercury Monitoring Provisions**

the laboratory performs the spike recovery study described in section 10.3 of appendix K to this attachment and repeats that procedure annually, ISO certification is not required.

### **1.5.5 Data Collection Period**

State, and provide the rationale for, the minimum acceptable data collection period ( *e.g.* , one day, one week, etc.) for the size of sorbent trap selected for the monitoring. Include in the discussion such factors as the Hg concentration in the stack gas, the capacity of the sorbent trap, and the minimum mass of Hg required for the analysis.

### **1.5.6 Relative Accuracy Test Audit Procedures**

Keep records of the procedures and details peculiar to the sorbent trap monitoring systems that are to be followed for relative accuracy test audits, such as sampling and analysis methods.

## **2. Frequency of Testing**

A summary chart showing each quality assurance test and the frequency at which each test is required is located at the end of this appendix in Figure 1.

### ***2.1 Daily Assessments***

Perform the following daily assessments to quality-assure the hourly data recorded by the monitoring systems during each period of unit operation, or, for a bypass stack or duct, each period in which emissions pass through the bypass stack or duct. These requirements are effective as of the date when the monitor or continuous emission monitoring system completes certification testing.

#### **2.1.1 Calibration Error Test**

Except as provided in section 2.1.1.2 of this appendix, perform the daily calibration error test of each gas monitoring system (including moisture monitoring systems consisting of wet- and dry-basis O<sub>2</sub> analyzers) according to the procedures in section 6.3.1 of appendix A to this attachment, and perform the daily calibration error test of each flow monitoring system according to the procedure in section 6.3.2 of appendix A to this attachment. When two measurement ranges (low and high) are required for a particular parameter, perform sufficient calibration error tests on each range to validate the data recorded on that range, according to the criteria in section 2.1.5 of this appendix.

***2.1.1.1 On-line Daily Calibration Error Tests.*** Except as provided in section 2.1.1.2 of this appendix, all daily calibration error tests must be performed while the unit is in operation at normal, stable conditions (i.e. “on-line”).

## **Attachment: Mercury Monitoring Provisions**

*2.1.1.2 Off-line Daily Calibration Error Tests.* Daily calibrations may be performed while the unit is not operating (i.e., “off-line”) and may be used to validate data for a monitoring system that meets the following conditions:

(1) An initial demonstration test of the monitoring system is successfully completed and the results are reported in the quarterly report required under 40 CFR 75.64. The initial demonstration test, hereafter called the “off-line calibration demonstration”, consists of an off-line calibration error test followed by an on-line calibration error test. Both the off-line and on-line portions of the off-line calibration demonstration must meet the calibration error performance specification in section 3.1 of appendix A of this attachment. Upon completion of the off-line portion of the demonstration, the zero and upscale monitor responses may be adjusted, but only toward the true values of the calibration gases or reference signals used to perform the test and only in accordance with the routine calibration adjustment procedures specified in the quality control program required under section 1 of appendix B to this attachment. Once these adjustments are made, no further adjustments may be made to the monitoring system until after completion of the on-line portion of the off-line calibration demonstration. Within 26 clock hours of the completion hour of the off-line portion of the demonstration, the monitoring system must successfully complete the first attempted calibration error test, i.e., the on-line portion of the demonstration.

(2) For each monitoring system that has passed the off-line calibration demonstration, off-line calibration error tests may be used on a limited basis to validate data, in accordance with paragraph (2) in section 2.1.5.1 of this appendix.

### **2.1.2 Daily Flow Interference Check**

Perform the daily flow monitor interference checks specified in section 2.2.2.2 of appendix A of this attachment while the unit is in operation at normal, stable conditions.

### **2.1.3 Additional Calibration Error Tests and Calibration Adjustments**

(a) In addition to the daily calibration error tests required under section 2.1.1 of this appendix, a calibration error test of a monitor shall be performed in accordance with section 2.1.1 of this appendix, as follows: whenever a daily calibration error test is failed; whenever a monitoring system is returned to service following repair or corrective maintenance that could affect the monitor's ability to accurately measure and record emissions data; or after making certain calibration adjustments, as described in this section. Except in the case of the routine calibration adjustments described in this section, data from the monitor are considered invalid until the required additional calibration error test has been successfully completed.

(b) Routine calibration adjustments of a monitor are permitted after any successful calibration error test. These routine adjustments shall be made so as to bring the monitor readings as close as practicable to the known tag values of the calibration gases or to the actual value of the flow monitor reference signals. An additional calibration error test is

## Attachment: Mercury Monitoring Provisions

required following routine calibration adjustments where the monitor's calibration has been physically adjusted (e.g., by turning a potentiometer) to verify that the adjustments have been made properly. An additional calibration error test is not required, however, if the routine calibration adjustments are made by means of a mathematical algorithm programmed into the data acquisition and handling system. The DEQ recommends that routine calibration adjustments be made, at a minimum, whenever the daily calibration error exceeds the limits of the applicable performance specification in appendix A to this attachment for the pollutant concentration monitor, CO<sub>2</sub> or O<sub>2</sub> monitor, or flow monitor.

(c) Additional (non-routine) calibration adjustments of a monitor are permitted prior to (but not during) linearity checks and RATAs and at other times, provided that an appropriate technical justification is included in the quality control program required under section 1 of this appendix. The allowable non-routine adjustments are as follows. The permittee may physically adjust the calibration of a monitor (e.g., by means of a potentiometer), provided that the post-adjustment zero and upscale responses of the monitor are within the performance specifications of the instrument given in section 3.1 of appendix A to this attachment. An additional calibration error test is required following such adjustments to verify that the monitor is operating within the performance specifications at both the zero and upscale calibration levels.

### 2.1.4 Data Validation

(a) An out-of-control period occurs when the calibration error of an SO<sub>2</sub> or NO<sub>x</sub> pollutant concentration monitor exceeds 5.0 percent of the span value, when the calibration error of a CO<sub>2</sub> or O<sub>2</sub> monitor (including O<sub>2</sub> monitors used to measure CO<sub>2</sub> emissions or percent moisture) exceeds 1.0 percent CO<sub>2</sub> or O<sub>2</sub>, or when the calibration error of a flow monitor or a moisture sensor exceeds 6.0 percent of the span value, which is twice the applicable specification of appendix A to this attachment. Notwithstanding, a differential pressure-type flow monitor for which the calibration error exceeds 6.0 percent of the span value shall not be considered out-of-control if  $|R - A|$ , the absolute value of the difference between the monitor response and the reference value in Equation A-6 of appendix A to this attachment, is  $< 0.02$  inches of water. In addition, an SO<sub>2</sub> or NO<sub>x</sub> monitor for which the calibration error exceeds 5.0 percent of the span value shall not be considered out-of-control if  $|R - A|$  in Equation A-6 does not exceed 5.0 ppm (for span values  $\leq 50$  ppm), or if  $|R - A|$  does not exceed 10.0 ppm (for span values  $> 50$  ppm, but  $\leq 200$  ppm). For a Hg monitor, an out-of-control period occurs when the calibration error exceeds 5.0% of the span value. Notwithstanding, the Hg monitor shall not be considered out-of-control if  $|R - A|$  in Equation A-6 does not exceed 1.0  $\mu\text{gm}/\text{scm}$ . The out-of-control period begins upon failure of the calibration error test and ends upon completion of a successful calibration error test. Note, that if a failed calibration, corrective action, and successful calibration error test occur within the same hour, emission data for that hour recorded by the monitor after the successful calibration error test may be used for reporting purposes, provided that two or more valid readings are obtained as required by 40 CFR 75.10. A NO<sub>x</sub>-diluent CEMS is considered out-of-control if the calibration error of either component monitor exceeds

## Attachment: Mercury Monitoring Provisions

twice the applicable performance specification in appendix A to this attachment. Emission data shall not be reported from an out-of-control monitor.

(b) An out-of-control period also occurs whenever interference of a flow monitor is identified. The out-of-control period begins with the hour of completion of the failed interference check and ends with the hour of completion of an interference check that is passed.

### 2.1.5 Quality Assurance of Data With Respect to Daily Assessments

When a monitoring system passes a daily assessment (i.e., daily calibration error test or daily flow interference check), data from that monitoring system are prospectively validated for 26 clock hours (i.e., 24 hours plus a 2-hour grace period) beginning with the hour in which the test is passed, unless another assessment (i.e. a daily calibration error test, an interference check of a flow monitor, a quarterly linearity check, a quarterly leak check, or a relative accuracy test audit) is failed within the 26-hour period.

*2.1.5.1 Data Invalidation with Respect to Daily Assessments.* The following specific rules apply to the invalidation of data with respect to daily assessments:

(1) Data from a monitoring system are invalid, beginning with the first hour following the expiration of a 26-hour data validation period or beginning with the first hour following the expiration of an 8-hour start-up grace period (as provided under section 2.1.5.2 of this appendix), if the required subsequent daily assessment has not been conducted.

(2) For a monitor that has passed the off-line calibration demonstration, a combination of on-line and off-line calibration error tests may be used to validate data from the monitor, as follows. For a particular unit (or stack) operating hour, data from a monitor may be validated using a successful off-line calibration error test if: (a) An on-line calibration error test has been passed within the previous 26 unit (or stack) operating hours; and (b) the 26 clock hour data validation window for the off-line calibration error test has not expired. If either of these conditions is not met, then the data from the monitor are invalid with respect to the daily calibration error test requirement. Data from the monitor shall remain invalid until the appropriate on-line or off-line calibration error test is successfully completed so that both conditions (a) and (b) are met.

(3) For units with two measurement ranges (low and high) for a particular parameter, when separate analyzers are used for the low and high ranges, a failed or expired calibration on one of the ranges does not affect the quality-assured data status on the other range. For a dual-range analyzer (i.e., a single analyzer with two measurement scales), a failed calibration error test on either the low or high scale results in an out-of-control period for the monitor. Data from the monitor remain invalid until corrective actions are taken and “hands-off” calibration error tests have been passed on both ranges. However, if the most recent calibration error test on the high scale was passed but has expired, while the low scale is up-to-date on its calibration error test requirements (or

## **Attachment: Mercury Monitoring Provisions**

vice-versa), the expired calibration error test does not affect the quality-assured status of the data recorded on the other scale.

*2.1.5.2 Daily Assessment Start-Up Grace Period.* For the purpose of quality assuring data with respect to a daily assessment (i.e. a daily calibration error test or a flow interference check), a start-up grace period may apply when a unit begins to operate after a period of non-operation. The start-up grace period for a daily calibration error test is independent of the start-up grace period for a daily flow interference check. To qualify for a start-up grace period for a daily assessment, there are two requirements:

- (1) The unit must have resumed operation after being in outage for 1 or more hours (i.e., the unit must be in a start-up condition) as evidenced by a change in unit operating time from zero in one clock hour to an operating time greater than zero in the next clock hour.
- (2) For the monitoring system to be used to validate data during the grace period, the previous daily assessment of the same kind must have been passed on-line within 26 clock hours prior to the last hour in which the unit operated before the outage. In addition, the monitoring system must be in-control with respect to quarterly and semi-annual or annual assessments.

If both of the above conditions are met, then a start-up grace period of up to 8 clock hours applies, beginning with the first hour of unit operation following the outage. During the start-up grace period, data generated by the monitoring system are considered quality-assured. For each monitoring system, a start-up grace period for a calibration error test or flow interference check ends when either: (1) a daily assessment of the same kind (i.e., calibration error test or flow interference check) is performed; or (2) 8 clock hours have elapsed (starting with the first hour of unit operation following the outage), whichever occurs first.

### **2.1.6 Data Recording**

Record and tabulate all calibration error test data according to month, day, clock-hour, and magnitude in either ppm, percent volume, or scfh. Program monitors that automatically adjust data to the corrected calibration values (e.g., microprocessor control) to record either: (1) The unadjusted concentration or flow rate measured in the calibration error test prior to resetting the calibration, or (2) the magnitude of any adjustment. Record the following applicable flow monitor interference check data: (1) Sample line/sensing port pluggage, and (2) malfunction of each RTD, transceiver, or equivalent.

### **2.2 Quarterly Assessments**

For each primary and redundant backup monitor or monitoring system, perform the following quarterly assessments. This requirement is applies as of the calendar quarter following the calendar quarter in which the monitor or continuous emission monitoring system is provisionally certified.

## **Attachment: Mercury Monitoring Provisions**

### **2.2.1 Linearity Check**

Unless a particular monitor (or monitoring range) is exempted under this paragraph or under section 6.2 of appendix A to this attachment, perform a linearity check, in accordance with the procedures in section 6.2 of appendix A to this attachment, for each primary and redundant backup SO<sub>2</sub>, Hg, and NO<sub>x</sub> pollutant concentration monitor and each primary and redundant backup CO<sub>2</sub> or O<sub>2</sub> monitor (including O<sub>2</sub> monitors used to measure CO<sub>2</sub> emissions or to continuously monitor moisture) at least once during each QA operating quarter, as defined in 40 CFR 72.2. For Hg monitors, perform the linearity checks using elemental Hg standards. Alternatively, you may perform 3-level system integrity checks at the same three calibration gas levels ( *i.e.* , low, mid, and high), using a NIST-traceable source of oxidized Hg. If you choose this option, the performance specification in section 3.2(c)(3) of appendix A to this attachment must be met at each gas level. For units using both a low and high span value, a linearity check is required only on the range(s) used to record and report emission data during the QA operating quarter. Conduct the linearity checks no less than 30 days apart, to the extent practicable. The data validation procedures in section 2.2.3(e) of this appendix shall be followed.

### **2.2.2 Leak Check**

For differential pressure flow monitors, perform a leak check of all sample lines (a manual check is acceptable) at least once during each QA operating quarter. For this test, the unit does not have to be in operation. Conduct the leak checks no less than 30 days apart, to the extent practicable. If a leak check is failed, follow the applicable data validation procedures in section 2.2.3(g) of this appendix.

### **2.2.3 Data Validation**

(a) A linearity check shall not be commenced if the monitoring system is operating out-of-control with respect to any of the daily or semiannual quality assurance assessments required by sections 2.1 and 2.3 of this appendix or with respect to the additional calibration error test requirements in section 2.1.3 of this appendix.

(b) Each required linearity check shall be done according to paragraph (b)(1), (b)(2) or (b)(3) of this section:

(1) The linearity check may be done “cold,” *i.e.*, with no corrective maintenance, repair, calibration adjustments, re-linearization or reprogramming of the monitor prior to the test.

(2) The linearity check may be done after performing only the routine or non-routine calibration adjustments described in section 2.1.3 of this appendix at the various calibration gas levels (zero, low, mid or high), but no other corrective maintenance, repair, re-linearization or reprogramming of the monitor. Trial gas injection runs may be performed after the calibration adjustments and additional adjustments within the allowable limits in section 2.1.3 of this appendix may be made prior to the linearity



## **Attachment: Mercury Monitoring Provisions**

check, as necessary, to optimize the performance of the monitor. The trial gas injections need not be reported, provided that they meet the specification for trial gas injections in 40 CFR 75.20(b)(3)(vii)(E)(1). However, if, for any trial injection, the specification in 40 CFR 75.20(b)(3)(vii)(E)(1) is not met, the trial injection shall be counted as an aborted linearity check.

(3) The linearity check may be done after repair, corrective maintenance or reprogramming of the monitor. In this case, the monitor shall be considered out-of-control from the hour in which the repair, corrective maintenance or reprogramming is commenced until the linearity check has been passed. Alternatively, the data validation procedures and associated timelines in 40 CFR 75.20(b)(3)(ii) through (ix) may be followed upon completion of the necessary repair, corrective maintenance, or reprogramming. If the procedures in 40 CFR 75.20(b)(3) are used, the words “quality assurance” apply instead of the word “recertification”.

(c) Once a linearity check has been commenced, the test shall be done hands-off. That is, no adjustments of the monitor are permitted during the linearity test period, other than the routine calibration adjustments following daily calibration error tests, as described in section 2.1.3 of this appendix. If a routine daily calibration error test is performed and passed just prior to a linearity test (or during a linearity test period) and a mathematical correction factor is automatically applied by the DAHS, the correction factor shall be applied to all subsequent data recorded by the monitor, including the linearity test data.

(d) If a daily calibration error test is failed during a linearity test period, prior to completing the test, the linearity test must be repeated. Data from the monitor are invalidated prospectively from the hour of the failed calibration error test until the hour of completion of a subsequent successful calibration error test. The linearity test shall not be commenced until the monitor has successfully completed a calibration error test.

(e) An out-of-control period occurs when a linearity test is failed (i.e., when the error in linearity at any of the three concentrations in the quarterly linearity check (or any of the six concentrations, when both ranges of a single analyzer with a dual range are tested) exceeds the applicable specification in section 3.2 of appendix A to this attachment) or when a linearity test is aborted due to a problem with the monitor or monitoring system. For a NO<sub>x</sub>-diluent continuous emission monitoring system, the system is considered out-of-control if either of the component monitors exceeds the applicable specification in section 3.2 of appendix A to this attachment or if the linearity test of either component is aborted due to a problem with the monitor. The out-of-control period begins with the hour of the failed or aborted linearity check and ends with the hour of completion of a satisfactory linearity check following corrective action and/or monitor repair, unless the option in paragraph (b)(3) of this section to use the data validation procedures and associated timelines in 40 CFR 75.20(b)(3)(ii) through (ix) has been selected, in which case the beginning and end of the out-of-control period shall be determined in accordance with 40 CFR 75.20(b)(3)(vii)(A) and (B). For a dual-range analyzer, “hands-off” linearity checks must be passed on both measurement scales to end the out-of-control period. Note

## **Attachment: Mercury Monitoring Provisions**

that a monitor shall not be considered out-of-control when a linearity test is aborted for a reason unrelated to the monitor's performance (e.g., a forced unit outage).

(f) No more than four successive calendar quarters shall elapse after the quarter in which a linearity check of a monitor or monitoring system (or range of a monitor or monitoring system) was last performed without a subsequent linearity test having been conducted. If a linearity test has not been completed by the end of the fourth calendar quarter since the last linearity test, then the linearity test must be completed within a 168 unit operating hour or stack operating hour "grace period" (as provided in section 2.2.4 of this appendix) following the end of the fourth successive elapsed calendar quarter, or data from the CEMS (or range) will become invalid.

(g) An out-of-control period also occurs when a flow monitor sample line leak is detected. The out-of-control period begins with the hour of the failed leak check and ends with the hour of a satisfactory leak check following corrective action.

(h) For each monitoring system, report the results of all completed and partial linearity tests that affect data validation (i.e., all completed, passed linearity checks; all completed, failed linearity checks; and all linearity checks aborted due to a problem with the monitor, including trial gas injections counted as failed test attempts under paragraph (b)(2) of this section or under 40 CFR 75.20(b)(3)(vii)(F)), in the quarterly report required under 40 CFR 75.64. Note that linearity attempts which are aborted or invalidated due to problems with the reference calibration gases or due to operational problems with the CFB boilers need not be reported. Such partial tests do not affect the validation status of emission data recorded by the monitor. A record of all linearity tests, trial gas injections and test attempts (whether reported or not) must be kept on-site as part of the official test log for each monitoring system.

### **2.2.4 Linearity and Leak Check Grace Period**

(a) When a required linearity test or flow monitor leak check has not been completed by the end of the QA operating quarter in which it is due or if, due to infrequent operation of a unit or infrequent use of a required high range of a monitor or monitoring system, four successive calendar quarters have elapsed after the quarter in which a linearity check of a monitor or monitoring system (or range) was last performed without a subsequent linearity test having been done, the permittee has a grace period of 168 consecutive unit operating hours, as defined in 40 CFR 72.2 (or, for monitors installed on common stacks or bypass stacks, 168 consecutive stack operating hours, as defined in 40 CFR 72.2) in which to perform a linearity test or leak check of that monitor or monitoring system (or range). The grace period begins with the first unit or stack operating hour following the calendar quarter in which the linearity test was due. Data validation during a linearity or leak check grace period shall be done in accordance with the applicable provisions in section 2.2.3 of this appendix.

(b) If, at the end of the 168 unit (or stack) operating hour grace period, the required linearity test or leak check has not been completed, data from the monitoring system (or

## Attachment: Mercury Monitoring Provisions

range) shall be invalid, beginning with the first unit operating hour following the expiration of the grace period. Data from the monitoring system (or range) remain invalid until the hour of completion of a subsequent successful hands-off linearity test or leak check of the monitor or monitoring system (or range). Note that when a linearity test or a leak check is conducted within a grace period for the purpose of satisfying the linearity test or leak check requirement from a previous QA operating quarter, the results of that linearity test or leak check may only be used to meet the linearity check or leak check requirement of the previous quarter, not the quarter in which the missed linearity test or leak check is completed.

### 2.2.5 Flow-to-Load Ratio or Gross Heat Rate Evaluation

(a) *Applicability and methodology.* Unless exempted from the flow-to-load ratio test under section 7.8 of appendix A to this attachment, the permittee shall, for each flow rate monitoring system installed on each unit, common stack or multiple stack, evaluate the flow-to-load ratio quarterly, i.e., for each QA operating quarter (as defined in 40 CFR 72.2). At the end of each QA operating quarter, the permittee shall use Equation B-1 to calculate the flow-to-load ratio for every hour during the quarter in which: the unit (or combination of units, for a common stack) operated within  $\pm 10.0$  percent of  $L_{avg}$ , the average load during the most recent normal-load flow RATA; and a quality-assured hourly average flow rate was obtained with a certified flow rate monitor. Alternatively, for the reasons stated in paragraphs (c)(1) through (c)(6) of this section, the permittee may exclude from the data analysis certain hours within  $\pm 10.0$  percent of  $L_{avg}$  and may calculate  $R_h$  values for only the remaining hours.

$$R_h = \frac{Q_h}{L_h} \times 10^{-5} \quad (\text{Eq. B-1})$$

Where:

$R_h$  = Hourly value of the flow-to-load ratio, scfh/megawatts, scfh/1000 lb/hr of steam, or scfh/(mmBtu/hr thermal output).

$Q_h$  = Hourly stack gas volumetric flow rate, as measured by the flow rate monitor, scfh.

$L_h$  = Hourly unit load, megawatts, 1000 lb/hr of steam, or mmBtu/hr thermal output; must be within  $\pm 10.0$  percent of  $L_{avg}$  during the most recent normal-load flow RATA.

(1) In Equation B-1, the permittee may use either bias-adjusted flow rates or unadjusted flow rates, provided that all of the ratios are calculated the same way. For a common stack,  $L_h$  shall be the sum of the hourly operating loads of all units that discharge through the stack. For a unit that discharges its emissions through multiple stacks or that monitors its emissions in multiple breechings,  $Q_h$  will be either the combined hourly volumetric flow rate for all of the stacks or ducts (if the test is done on a unit basis) or the hourly flow rate through each stack individually (if the test is performed separately for each stack). For a unit with a multiple stack discharge configuration consisting of a main stack

## Attachment: Mercury Monitoring Provisions

and a bypass stack, each of which has a certified flow monitor (e.g., a unit with a wet SO<sub>2</sub> scrubber), calculate the hourly flow-to-load ratios separately for each stack. Round off each value of  $R_h$  to two decimal places.

(2) Alternatively, the permittee may calculate the hourly gross heat rates (GHR) in lieu of the hourly flow-to-load ratios. The hourly GHR shall be determined only for those hours in which quality-assured flow rate data and diluent gas (CO<sub>2</sub> or O<sub>2</sub>) concentration data are both available from a certified monitor or monitoring system or reference method. If this option is selected, calculate each hourly GHR value as follows:

$$(GHR)_h = \frac{(\text{Heat Input})_h}{L_h} \times 1000 \quad (\text{Eq. B-1a})$$

where:

$(GHR)_h$  = Hourly value of the gross heat rate, Btu/kwh, Btu/lb steam load, or 1000 mmBtu heat input/mmBtu thermal output.

$(\text{Heat Input})_h$  = Hourly heat input, as determined from the quality-assured flow rate and diluent data, using the applicable equation in appendix F to this attachment, mmBtu/hr.

$L_h$  = Hourly unit load, megawatts, 1000 lb/hr of steam, or mmBtu/hr thermal output; must be within + 10.0 percent of  $L_{avg}$  during the most recent normal-load flow RATA.

(3) In Equation B-1a, the permittee may either use bias-adjusted flow rates or unadjusted flow rates in the calculation of  $(\text{Heat Input})_h$ , provided that all of the heat input rate values are determined in the same manner.

(4) The permittee shall evaluate the calculated hourly flow-to-load ratios (or gross heat rates) as follows. A separate data analysis shall be performed for each primary and each redundant backup flow rate monitor used to record and report data during the quarter. Each analysis shall be based on a minimum of 168 acceptable recorded hourly average flow rates (i.e., at loads within  $\pm 10$  percent of  $L_{avg}$ ). When two RATA load levels are designated as normal, the analysis shall be performed at the higher load level, unless there are fewer than 168 acceptable data points available at that load level, in which case the analysis shall be performed at the lower load level. If, for a particular flow monitor, fewer than 168 acceptable hourly flow-to-load ratios (or GHR values) are available at any of the load levels designated as normal, a flow-to-load (or GHR) evaluation is not required for that monitor for that calendar quarter.

(5) For each flow monitor, use Equation B-2 in this appendix to calculate  $E_h$ , the absolute percentage difference between each hourly  $R_h$  value and  $R_{ref}$ , the reference value of the flow-to-load ratio, as determined in accordance with section 7.7 of appendix A to this attachment. Note that  $R_{ref}$  shall always be based upon the most recent normal-load RATA, even if that RATA was performed in the calendar quarter being evaluated.

## Attachment: Mercury Monitoring Provisions

$$E_h = \frac{|R_{ref} - R_h|}{R_{ref}} \times 100 \quad (\text{Eq. B-2})$$

where:

$E_h$  = Absolute percentage difference between the hourly average flow-to-load ratio and the reference value of the flow-to-load ratio at normal load.

$R_h$  = The hourly average flow-to-load ratio, for each flow rate recorded at a load level within  $\pm 10.0$  percent of  $L_{avg}$ .

$R_{ref}$  = The reference value of the flow-to-load ratio from the most recent normal-load flow RATA, determined in accordance with section 7.7 of appendix A to this attachment.

(6) Equation B-2 shall be used in a consistent manner. That is, use  $R_{ref}$  and  $R_h$  if the flow-to-load ratio is being evaluated, and use  $(GHR)_{ref}$  and  $(GHR)_h$  if the gross heat rate is being evaluated. Finally, calculate  $E_f$ , the arithmetic average of all of the hourly  $E_h$  values. The permittee shall report the results of each quarterly flow-to-load (or gross heat rate) evaluation, as determined from Equation B-2, in the electronic quarterly report required under 40 CFR 75.64.

(b) *Acceptable results.* The results of a quarterly flow-to-load (or gross heat rate) evaluation are acceptable, and no further action is required, if the calculated value of  $E_f$  is less than or equal to: (1) 15.0 percent, if  $L_{avg}$  for the most recent normal-load flow RATA is  $\geq 60$  megawatts (or  $\geq 500$  klb/hr of steam) and if unadjusted flow rates were used in the calculations; or (2) 10.0 percent, if  $L_{avg}$  for the most recent normal-load flow RATA is  $\geq 60$  megawatts (or  $\geq 500$  klb/hr of steam) and if bias-adjusted flow rates were used in the calculations; or (3) 20.0 percent, if  $L_{avg}$  for the most recent normal-load flow RATA is  $< 60$  megawatts (or  $< 500$  klb/hr of steam) and if unadjusted flow rates were used in the calculations; or (4) 15.0 percent, if  $L_{avg}$  for the most recent normal-load flow RATA is  $< 60$  megawatts (or  $< 500$  klb/hr of steam) and if bias-adjusted flow rates were used in the calculations. If  $E_f$  is above these limits, the permittee shall either: implement Option 1 in section 2.2.5.1 of this appendix; or perform a RATA in accordance with Option 2 in section 2.2.5.2 of this appendix; or re-examine the hourly data used for the flow-to-load or GHR analysis and recalculate  $E_f$ , after excluding all non-representative hourly flow rates. If  $E_f$  is above these limits, the permittee shall either: implement Option 1 in section 2.2.5.1 of this appendix; perform a RATA in accordance with Option 2 in section 2.2.5.2 of this appendix; or (if applicable) re-examine the hourly data used for the flow-to-load or GHR analysis and recalculate  $E_f$ , after excluding all non-representative hourly flow rates, as provided in paragraph (c) of this section.

(c) *Recalculation of  $E_f$ .* If the permittee did not exclude any hours within  $\pm 10$  percent of  $L_{avg}$  from the original data analysis and chooses to recalculate  $E_f$ , the flow rates for the following hours are considered non-representative and may be excluded from the data analysis:

## Attachment: Mercury Monitoring Provisions

- (1) Any hour in which the type of fuel combusted was different from the fuel burned during the most recent normal-load RATA. For purposes of this determination, the type of fuel is different if the fuel is in a different state of matter (i.e., solid, liquid, or gas) than is the fuel burned during the RATA or if the fuel is a different classification of coal (e.g., bituminous versus sub-bituminous). Also, for units that co-fire different types of fuels, if the reference RATA was done while co-firing, then hours in which a single fuel was combusted may be excluded from the data analysis as different fuel hours (and vice-versa for co-fired hours, if the reference RATA was done while combusting only one type of fuel);
- (2) For a unit that is equipped with an SO<sub>2</sub> scrubber and which always discharges its flue gases to the atmosphere through a single stack, any hour in which the SO<sub>2</sub> scrubber was bypassed;
- (3) Any hour in which "ramping" occurred, i.e., the hourly load differed by more than  $\pm 15.0$  percent from the load during the preceding hour or the subsequent hour;
- (4) For a unit with a multiple stack discharge configuration consisting of a main stack and a bypass stack, any hour in which the flue gases were discharged through both stacks;
- (5) If a normal-load flow RATA was performed and passed during the quarter being analyzed, any hour prior to completion of that RATA; and
- (6) If a problem with the accuracy of the flow monitor was discovered during the quarter and was corrected (as evidenced by passing the abbreviated flow-to-load test in section 2.2.5.3 of this appendix), any hour prior to completion of the abbreviated flow-to-load test.
- (7) After identifying and excluding all non-representative hourly data in accordance with paragraphs (c)(1) through (6) of this section, the permittee may analyze the remaining data a second time. At least 168 representative hourly ratios or GHR values must be available to perform the analysis; otherwise, the flow-to-load (or GHR) analysis is not required for that monitor for that calendar quarter.
- (8) If, after re-analyzing the data,  $E_f$  meets the applicable limit in paragraph (b)(1), (b)(2), (b)(3), or (b)(4) of this section, no further action is required. If, however,  $E_f$  is still above the applicable limit, data from the monitor shall be declared out-of-control, beginning with the first unit operating hour following the quarter in which  $E_f$  exceeded the applicable limit. Alternatively, if a probationary calibration error test is performed and passed according to 40 CFR 75.20(b)(3)(ii), data from the monitor may be declared conditionally valid following the quarter in which  $E_f$  exceeded the applicable limit. The permittee shall then either implement Option 1 in section 2.2.5.1 of this appendix or Option 2 in section 2.2.5.2 of this appendix.

## **Attachment: Mercury Monitoring Provisions**

### **2.2.5.1 Option 1**

Within 14 unit operating days of the end of the calendar quarter for which the  $E_f$  value is above the applicable limit, investigate and troubleshoot the applicable flow monitor(s). Evaluate the results of each investigation as follows:

(a) If the investigation fails to uncover a problem with the flow monitor, a RATA shall be performed in accordance with Option 2 in section 2.2.5.2 of this appendix.

(b) If a problem with the flow monitor is identified through the investigation (including the need to re-linearize the monitor by changing the polynomial coefficients or K factor(s)), data from the monitor are considered invalid back to the first unit operating hour after the end of the calendar quarter for which  $E_f$  was above the applicable limit. If the option to use conditional data validation was selected under section 2.2.5(c)(8) of this appendix, all conditionally valid data shall be invalidated, back to the first unit operating hour after the end of the calendar quarter for which  $E_f$  was above the applicable limit. Corrective actions shall be taken. All corrective actions (e.g., non-routine maintenance, repairs, major component replacements, re-linearization of the monitor, etc.) shall be documented in the operation and maintenance records for the monitor. The permittee then shall either complete the abbreviated flow-to-load test in section 2.2.5.3 of this appendix, or, if the corrective action taken has required relinearization of the flow monitor, shall perform a 3-load RATA. The conditional data validation procedures in 40 CFR 75.20(b)(3) may be applied to the 3-load RATA.

### **2.2.5.2 Option 2**

Perform a single-load RATA (at a load designated as normal under section 6.5.2.1 of appendix A to this attachment) of each flow monitor for which  $E_f$  is outside of the applicable limit. If the RATA is passed hands-off, in accordance with section 2.3.2(c) of this appendix, no further action is required and the out-of-control period for the monitor ends at the date and hour of completion of a successful RATA, unless the option to use conditional data validation was selected under section 2.2.5(c)(8) of this appendix. In that case, all conditionally valid data from the monitor are considered to be quality-assured, back to the first unit operating hour following the end of the calendar quarter for which the  $E_f$  value was above the applicable limit. If the RATA is failed, all data from the monitor shall be invalidated, back to the first unit operating hour following the end of the calendar quarter for which the  $E_f$  value was above the applicable limit. Data from the monitor remain invalid until the required RATA has been passed. Alternatively, following a failed RATA and corrective actions, the conditional data validation procedures of 40 CFR 75.20(b)(3) may be used until the RATA has been passed. If the corrective actions taken following the failed RATA included adjustment of the polynomial coefficients or K-factor(s) of the flow monitor, a 3-level RATA is required, except as otherwise specified in section 2.3.1.3 of this appendix.

## Attachment: Mercury Monitoring Provisions

### 2.2.5.3 Abbreviated Flow-to-Load Test

(a) The following abbreviated flow-to-load test may be performed after any documented repair, component replacement, or other corrective maintenance to a flow monitor (except for changes affecting the linearity of the flow monitor, such as adjusting the flow monitor coefficients or K factor(s)) to demonstrate that the repair, replacement, or other maintenance has not significantly affected the monitor's ability to accurately measure the stack gas volumetric flow rate. Data from the monitoring system are considered invalid from the hour of commencement of the repair, replacement, or maintenance until either the hour in which the abbreviated flow-to-load test is passed, or the hour in which a probationary calibration error test is passed following completion of the repair, replacement, or maintenance and any associated adjustments to the monitor. If the latter option is selected, the abbreviated flow-to-load test shall be completed within 168 unit operating hours of the probationary calibration error test (or, for peaking units, within 30 unit operating days, if that is less restrictive). Data from the monitor are considered to be conditionally valid (as defined in 40 CFR 72.2), beginning with the hour of the probationary calibration error test.

(b) Operate the unit(s) in such a way as to reproduce, as closely as practicable, the exact conditions at the time of the most recent normal-load flow RATA. To achieve this, it is recommended that the load be held constant to within  $\pm 10.0$  percent of the average load during the RATA and that the diluent gas ( $\text{CO}_2$  or  $\text{O}_2$ ) concentration be maintained within  $\pm 0.5$  percent  $\text{CO}_2$  or  $\text{O}_2$  of the average diluent concentration during the RATA. For common stacks, to the extent practicable, use the same combination of units and load levels that were used during the RATA. When the process parameters have been set, record a minimum of six and a maximum of 12 consecutive hourly average flow rates, using the flow monitor(s) for which  $E_f$  was outside the applicable limit. For peaking units, a minimum of three and a maximum of 12 consecutive hourly average flow rates are required. Also record the corresponding hourly load values and, if applicable, the hourly diluent gas concentrations. Calculate the flow-to-load ratio (or GHR) for each hour in the test hour period, using Equation B-1 or B-1a. Determine  $E_h$  for each hourly flow-to-load ratio (or GHR), using Equation B-2 of this appendix and then calculate  $E_f$ , the arithmetic average of the  $E_h$  values.

(c) The results of the abbreviated flow-to-load test shall be considered acceptable, and no further action is required if the value of  $E_f$  does not exceed the applicable limit specified in section 2.2.5 of this appendix. All conditionally valid data recorded by the flow monitor shall be considered quality-assured, beginning with the hour of the probationary calibration error test that preceded the abbreviated flow-to-load test (if applicable). However, if  $E_f$  is outside the applicable limit, all conditionally valid data recorded by the flow monitor (if applicable) shall be considered invalid back to the hour of the probationary calibration error test that preceded the abbreviated flow-to-load test, and a single-load RATA is required in accordance with section 2.2.5.2 of this appendix. If the flow monitor must be re-linearized, however, a 3-load RATA is required.



## Attachment: Mercury Monitoring Provisions

### 2.3 Semiannual and Annual Assessments

For each primary and redundant backup monitoring system, perform relative accuracy assessments either semiannually or annually, as specified in section 2.3.1.1 or 2.3.1.2 of this appendix, for the type of test and the performance achieved. This requirement applies as of the calendar quarter following the calendar quarter in which the monitoring system is provisionally certified. A summary chart showing the frequency with which a relative accuracy test audit must be performed, depending on the accuracy achieved, is located at the end of this appendix in Figure 2.

#### 2.3.1 Relative Accuracy Test Audit (RATA)

##### 2.3.1.1 Standard RATA Frequencies

(a) Except for Hg monitoring systems and as otherwise specified in 40 CFR 75.21(a)(6) or (a)(7) or in section 2.3.1.2 of this appendix, perform relative accuracy test audits semiannually, *i.e.*, once every two successive QA operating quarters (as defined in 40 CFR 72.2) for each primary and redundant backup SO<sub>2</sub> pollutant concentration monitor, flow monitor, CO<sub>2</sub> emissions concentration monitor (including O<sub>2</sub> monitors used to determine CO<sub>2</sub> emissions), CO<sub>2</sub> or O<sub>2</sub> diluent monitor used to determine heat input, moisture monitoring system, NO<sub>x</sub> concentration monitoring system, NO<sub>x</sub>-diluent CEMS, or SO<sub>2</sub>-diluent CEMS. For each primary and redundant backup Hg concentration monitoring system and each sorbent trap monitoring system, RATAs shall be performed annually, *i.e.*, once every four successive QA operating quarters (as defined in 40 CFR 72.2). A calendar quarter that does not qualify as a QA operating quarter shall be excluded in determining the deadline for the next RATA. No more than eight successive calendar quarters shall elapse after the quarter in which a RATA was last performed without a subsequent RATA having been conducted. If a RATA has not been completed by the end of the eighth calendar quarter since the quarter of the last RATA, then the RATA must be completed within a 720 unit (or stack) operating hour grace period (as provided in section 2.3.3 of this appendix) following the end of the eighth successive elapsed calendar quarter, or data from the CEMS will become invalid.

(b) The relative accuracy test audit frequency of a CEMS may be reduced, as specified in section 2.3.1.2 of this appendix, for primary or redundant backup monitoring systems which qualify for less frequent testing. Perform all required RATAs in accordance with the applicable procedures and provisions in sections 6.5 through 6.5.2.2 of appendix A to this attachment and sections 2.3.1.3 and 2.3.1.4 of this appendix.

##### 2.3.1.2 Reduced RATA Frequencies

Relative accuracy test audits of primary and redundant backup SO<sub>2</sub> pollutant concentration monitors, CO<sub>2</sub> pollutant concentration monitors (including O<sub>2</sub> monitors used to determine CO<sub>2</sub> emissions), CO<sub>2</sub> or O<sub>2</sub> diluent monitors used to determine heat input, moisture monitoring systems, NO<sub>x</sub> concentration monitoring systems, flow monitors, NO<sub>x</sub>-diluent monitoring systems or SO<sub>2</sub>-diluent monitoring systems may be

## Attachment: Mercury Monitoring Provisions

performed annually (i.e., once every four successive QA operating quarters, rather than once every two successive QA operating quarters) if any of the following conditions are met for the specific monitoring system involved:

- (a) The relative accuracy during the audit of an SO<sub>2</sub> or CO<sub>2</sub> pollutant concentration monitor (including an O<sub>2</sub> pollutant monitor used to measure CO<sub>2</sub> using the procedures in appendix F to this attachment), or of a CO<sub>2</sub> or O<sub>2</sub> diluent monitor used to determine heat input, or of a NO<sub>x</sub> concentration monitoring system, or of a NO<sub>x</sub>-diluent monitoring system, or of an SO<sub>2</sub>-diluent continuous emissions monitoring system is  $\leq 7.5$  percent;
- (b) [Reserved]
- (c) The relative accuracy during the audit of a flow monitor is  $\leq 7.5$  percent at each operating level tested;
- (d) For low flow ( $\leq 10.0$  fps, as measured by the reference method during the RATA) stacks/ducts, when the flow monitor fails to achieve a relative accuracy  $\leq 7.5$  percent during the audit, but the monitor mean value, calculated using Equation A-7 in appendix A to this attachment and converted back to an equivalent velocity in standard feet per second (fps), is within  $\pm 1.5$  fps of the reference method mean value, converted to an equivalent velocity in fps;
- (e) For low SO<sub>2</sub> or NO<sub>x</sub> emitting units (average SO<sub>2</sub> or NO<sub>x</sub> reference method concentrations  $\leq 250$  ppm) during the RATA, when an SO<sub>2</sub> pollutant concentration monitor or NO<sub>x</sub> concentration monitoring system fails to achieve a relative accuracy  $\leq 7.5$  percent during the audit, but the monitor mean value from the RATA is within  $\pm 12$  ppm of the reference method mean value;
- (f) For units with low NO<sub>x</sub> emission rates (average NO<sub>x</sub> emission rate measured by the reference method during the RATA  $\leq 0.200$  lb/mmBtu), when a NO<sub>x</sub>-diluent continuous emission monitoring system fails to achieve a relative accuracy  $\leq 7.5$  percent, but the monitoring system mean value from the RATA, calculated using Equation A-7 in appendix A to this attachment, is within  $\pm 0.015$  lb/mmBtu of the reference method mean value;
- (g) [Reserved]
- (h) For a CO<sub>2</sub> or O<sub>2</sub> monitor, when the mean difference between the reference method values from the RATA and the corresponding monitor values is within  $\pm 0.7$  percent CO<sub>2</sub> or O<sub>2</sub>; and
- (i) When the relative accuracy of a continuous moisture monitoring system is  $\leq 7.5$  percent or when the mean difference between the reference method values from the RATA and the corresponding monitoring system values is within  $\pm 1.0$  percent H<sub>2</sub>O.

## **Attachment: Mercury Monitoring Provisions**

### **2.3.1.3 RATA Load (or Operating) Levels and Additional RATA Requirements**

(a) For SO<sub>2</sub> pollutant concentration monitors, CO<sub>2</sub> emissions concentration monitors (including O<sub>2</sub> monitors used to determine CO<sub>2</sub> emissions), CO<sub>2</sub> or O<sub>2</sub> diluent monitors used to determine heat input, NO<sub>x</sub> concentration monitoring systems, Hg concentration monitoring systems, sorbent trap monitoring systems, moisture monitoring systems, and NO<sub>x</sub>-diluent monitoring systems, the required semiannual or annual RATA tests shall be done at the load level (or operating level) designated as normal under section 6.5.2.1(d) of appendix A to this attachment. If two load levels (or operating levels) are designated as normal, the required RATA(s) may be done at either load level (or operating level).

(b) For flow monitors installed on peaking units and bypass stacks, and for flow monitors that qualify to perform only single-level RATAs under section 6.5.2(e) of appendix A to this attachment, all required semiannual or annual relative accuracy test audits shall be single-load (or single-level) audits at the normal load (or operating level), as defined in section 6.5.2.1(d) of appendix A to this attachment.

(c) For all other flow monitors, the RATAs shall be performed as follows:

(1) An annual 2-load (or 2-level) flow RATA shall be done at the two most frequently used load levels (or operating levels), as determined under section 6.5.2.1(d) of appendix A to this attachment, or (if applicable) at the operating levels determined under section 6.5.2(e) of appendix A to this attachment. Alternatively, a 3-load (or 3-level) flow RATA at the low, mid, and high load levels (or operating levels), as defined under section 6.5.2.1(b) of appendix A to this attachment, may be performed in lieu of the 2-load (or 2-level) annual RATA.

(2) If the flow monitor is on a semiannual RATA frequency, 2-load (or 2-level) flow RATAs and single-load (or single-level) flow RATAs at the normal load level (or normal operating level) may be performed alternately.

(3) A single-load (or single-level) annual flow RATA may be performed in lieu of the 2-load (or 2-level) RATA if the results of an historical load data analysis show that in the time period extending from the ending date of the last annual flow RATA to a date that is no more than 21 days prior to the date of the current annual flow RATA, the unit (or combination of units, for a common stack) has operated at a single load level (or operating level) (low, mid, or high), for  $\geq 85.0$  percent of the time. Alternatively, a flow monitor may qualify for a single-load (or single-level) RATA if the 85.0 percent criterion is met in the time period extending from the beginning of the quarter in which the last annual flow RATA was performed through the end of the calendar quarter preceding the quarter of current annual flow RATA.

(4) A 3-load (or 3-level) RATA, at the low-, mid-, and high-load levels (or operating levels), as determined under section 6.5.2.1 of appendix A to this attachment, shall be performed at least once every twenty consecutive calendar quarters, except for flow

## **Attachment: Mercury Monitoring Provisions**

monitors that are exempted from 3-load (or 3-level) RATA testing under section 6.5.2(b) or 6.5.2(e) of appendix A to this attachment.

(5) A 3-load (or 3-level) RATA is required whenever a flow monitor is re-linearized, *i.e.*, when its polynomial coefficients or K factor(s) are changed, except for flow monitors that are exempted from 3-load (or 3-level) RATA testing under section 6.5.2(b) or 6.5.2(e) of appendix A to this attachment. For monitors so exempted under section 6.5.2(b), a single-load flow RATA is required. For monitors so exempted under section 6.5.2(e), either a single-level RATA or a 2-level RATA is required, depending on the number of operating levels documented in the monitoring plan for the unit.

(6) For all multi-level flow audits, the audit points at adjacent load levels or at adjacent operating levels ( *e.g.*, mid and high) shall be separated by no less than 25.0 percent of the “range of operation,” as defined in section 6.5.2.1 of appendix A to this attachment.

(d) A RATA of a moisture monitoring system shall be performed whenever the coefficient, K factor or mathematical algorithm determined under section 6.5.7 of appendix A to this attachment is changed.

### **2.3.1.4 Number of RATA Attempts**

The permittee may perform as many RATA attempts as are necessary to achieve the desired relative accuracy test audit frequencies and/or bias adjustment factors. However, the data validation procedures in section 2.3.2 of this appendix must be followed.

### **2.3.2 Data Validation**

(a) A RATA shall not commence if the monitoring system is operating out-of-control with respect to any of the daily and quarterly quality assurance assessments required by sections 2.1 and 2.2 of this appendix or with respect to the additional calibration error test requirements in section 2.1.3 of this appendix.

(b) Each required RATA shall be done according to paragraphs (b)(1), (b)(2) or (b)(3) of this section:

(1) The RATA may be done “cold,” *i.e.*, with no corrective maintenance, repair, calibration adjustments, re-linearization or reprogramming of the monitoring system prior to the test.

(2) The RATA may be done after performing only the routine or non-routine calibration adjustments described in section 2.1.3 of this appendix at the zero and/or upscale calibration gas levels, but no other corrective maintenance, repair, re-linearization or reprogramming of the monitoring system. Trial RATA runs may be performed after the calibration adjustments and additional adjustments within the allowable limits in section 2.1.3 of this appendix may be made prior to the RATA, as necessary, to optimize the performance of the CEMS. The trial RATA runs need not be reported, provided that they

## Attachment: Mercury Monitoring Provisions

meet the specification for trial RATA runs in 40 CFR 75.20(b)(3)(vii)(E)( 2 ). However, if, for any trial run, the specification in 40 CFR 75.20(b)(3)(vii)(E)( 2 ) is not met, the trial run shall be counted as an aborted RATA attempt.

(3) The RATA may be done after repair, corrective maintenance, re-linearization or reprogramming of the monitoring system. In this case, the monitoring system shall be considered out-of-control from the hour in which the repair, corrective maintenance, re-linearization or reprogramming is commenced until the RATA has been passed. Alternatively, the data validation procedures and associated timelines in 40 CFR 40 CFR 75.20(b)(3)(ii) through (ix) may be followed upon completion of the necessary repair, corrective maintenance, re-linearization or reprogramming. If the procedures in 40 CFR 75.20(b)(3) are used, the words “quality assurance” apply instead of the word “recertification.”

(c) Once a RATA is commenced, the test must be done hands-off. No adjustment of the monitor's calibration is permitted during the RATA test period, other than the routine calibration adjustments following daily calibration error tests, as described in section 2.1.3 of this appendix. If a routine daily calibration error test is performed and passed just prior to a RATA (or during a RATA test period) and a mathematical correction factor is automatically applied by the DAHS, the correction factor shall be applied to all subsequent data recorded by the monitor, including the RATA test data. For 2-level and 3-level flow monitor audits, no linearization or reprogramming of the monitor is permitted in between load levels.

(d) For single-load (or single-level) RATAs, if a daily calibration error test is failed during a RATA test period, prior to completing the test, the RATA must be repeated. Data from the monitor are invalidated prospectively from the hour of the failed calibration error test until the hour of completion of a subsequent successful calibration error test. The subsequent RATA shall not be commenced until the monitor has successfully passed a calibration error test in accordance with section 2.1.3 of this appendix. Notwithstanding these requirements, when ASTM D6784-02 (incorporated by reference under 40 CFR 75.6) or EPA Method 29 in appendix A-8 to 40 CFR part 60 is used as the reference method for the RATA of a Hg CEMS, if a calibration error test of the CEMS is failed during a RATA test period, any test run(s) completed prior to the failed calibration error test need not be repeated; however, the RATA may not continue until a subsequent calibration error test of the Hg CEMS has been passed. For multiple-load (or multiple-level) flow RATAs, each load level (or operating level) is treated as a separate RATA ( *i.e.* , when a calibration error test is failed prior to completing the RATA at a particular load level (or operating level), only the RATA at that load level (or operating level) must be repeated; the results of any previously-passed RATA(s) at the other load level(s) (or operating level(s)) are unaffected, unless re-linearization of the monitor is required to correct the problem that caused the calibration failure, in which case a subsequent 3-load (or 3-level) RATA is required), except as otherwise provided in section 2.3.1.3(c)(5) of this appendix.

## **Attachment: Mercury Monitoring Provisions**

(e) For a RATA performed using the option in paragraph (b)(1) or (b)(2) of this section, if the RATA is failed (that is, if the relative accuracy exceeds the applicable specification in section 3.3 of appendix A to this attachment) or if the RATA is aborted prior to completion due to a problem with the CEMS, then the CEMS is out-of-control and all emission data from the CEMS are invalidated prospectively from the hour in which the RATA is failed or aborted. Data from the CEMS remain invalid until the hour of completion of a subsequent RATA that meets the applicable specification in section 3.3 of appendix A to this attachment. If the option in paragraph (b)(3) of this section to use the data validation procedures and associated timelines in 40 CFR 75.20(b)(3)(ii) through (b)(3)(ix) has been selected, the beginning and end of the out-of-control period shall be determined in accordance with 40 CFR 75.20(b)(3)(vii)(A) and (B). Note that when a RATA is aborted for a reason other than monitoring system malfunction ( *see* paragraph (h) of this section), this does not trigger an out-of-control period for the monitoring system.

(f) For a 2-level or 3-level flow RATA, if, at any load level (or operating level), a RATA is failed or aborted due to a problem with the flow monitor, the RATA at that load level (or operating level) must be repeated. The flow monitor is considered out-of-control and data from the monitor are invalidated from the hour in which the test is failed or aborted and remain invalid until the passing of a RATA at the failed load level (or operating level), unless the option in paragraph (b)(3) of this section to use the data validation procedures and associated timelines in 40 CFR 75.20(b)(3)(ii) through (b)(3)(ix) has been selected, in which case the beginning and end of the out-of-control period shall be determined in accordance with 40 CFR 75.20(b)(3)(vii)(A) and (B). Flow RATA(s) that were previously passed at the other load level(s) (or operating level(s)) do not have to be repeated unless the flow monitor must be re-linearized following the failed or aborted test. If the flow monitor is re-linearized, a subsequent 3-load (or 3-level) RATA is required, except as otherwise provided in section 2.3.1.3(c)(5) of this appendix.

(g) Data validation for failed RATAs for a CO<sub>2</sub> pollutant concentration monitor (or an O<sub>2</sub> monitor used to measure CO<sub>2</sub> emissions), a NO<sub>x</sub> pollutant concentration monitor, and a NO<sub>x</sub>-diluent monitoring system shall be done according to paragraphs (g)(1) and (g)(2) of this section:

(1) For a CO<sub>2</sub> pollutant concentration monitor (or an O<sub>2</sub> monitor used to measure CO<sub>2</sub> emissions) which also serves as the diluent component in a NO<sub>x</sub>-diluent monitoring system, if the CO<sub>2</sub> (or O<sub>2</sub>) RATA is failed, then both the CO<sub>2</sub> (or O<sub>2</sub>) monitor and the associated NO<sub>x</sub>-diluent system are considered out-of-control, beginning with the hour of completion of the failed CO<sub>2</sub> (or O<sub>2</sub>) monitor RATA, and continuing until the hour of completion of subsequent hands-off RATAs which demonstrate that both systems have met the applicable relative accuracy specifications in sections 3.3.2 and 3.3.3 of appendix A to this attachment, unless the option in paragraph (b)(3) of this section to use the data validation procedures and associated timelines in 40 CFR 75.20(b)(3)(ii) through (b)(3)(ix) has been selected, in which case the beginning and end of the out-of-control period shall be determined in accordance with 40 CFR 75.20(b)(3)(vii)(A) and (B).

## **Attachment: Mercury Monitoring Provisions**

(2) This paragraph (g)(2) applies only to a NO<sub>x</sub> pollutant concentration monitor that serves both as the NO<sub>x</sub> component of a NO<sub>x</sub> concentration monitoring system (to measure NO<sub>x</sub> mass emissions) and as the NO<sub>x</sub> component in a NO<sub>x</sub>-diluent monitoring system (to measure NO<sub>x</sub> emission rate in lb/mmBtu). If the RATA of the NO<sub>x</sub> concentration monitoring system is failed, then both the NO<sub>x</sub> concentration monitoring system and the associated NO<sub>x</sub>-diluent monitoring system are considered out-of-control, beginning with the hour of completion of the failed NO<sub>x</sub> concentration RATA, and continuing until the hour of completion of subsequent hands-off RATAs which demonstrate that both systems have met the applicable relative accuracy specifications in sections 3.3.2 and 3.3.7 of appendix A to this attachment, unless the option in paragraph (b)(3) of this section to use the data validation procedures and associated timelines in 40 CFR 75.20(b)(3)(ii) through (b)(3)(ix) has been selected, in which case the beginning and end of the out-of-control period shall be determined in accordance with 40 CFR 75.20(b)(3)(vii)(A) and (B).

(h) For each monitoring system, report the results of all completed and partial RATAs that affect data validation (i.e., all completed, passed RATAs; all completed, failed RATAs; and all RATAs aborted due to a problem with the CEMS, including trial RATA runs counted as failed test attempts under paragraph (b)(2) of this section or under 40 CFR 75.20(b)(3)(vii)(F)) in the quarterly report required under 40 CFR 75.64. Note that RATA attempts that are aborted or invalidated due to problems with the reference method or due to operational problems with the CFB boilers need not be reported. Such runs do not affect the validation status of emission data recorded by the CEMS. However, a record of all RATAs, trial RATA runs and RATA attempts (whether reported or not) must be kept on-site as part of the official test log for each monitoring system.

(i) Each time that a hands-off RATA of an SO<sub>2</sub> pollutant concentration monitor, a NO<sub>x</sub>-diluent monitoring system, a NO<sub>x</sub> concentration monitoring system, a Hg concentration monitoring system, a sorbent trap monitoring system, or a flow monitor is passed, perform a bias test in accordance with section 7.6.4 of appendix A to this attachment. Apply the appropriate bias adjustment factor to the reported SO<sub>2</sub>, Hg, NO<sub>x</sub>, or flow rate data, in accordance with section 7.6.5 of appendix A to this attachment.

(j) Failure of the bias test does not result in the monitoring system being out-of-control.

### **2.3.3 RATA Grace Period**

(a) The permittee has a grace period of 720 consecutive unit operating hours, as defined in 40 CFR 72.2 (or, for CEMS installed on common stacks or bypass stacks, 720 consecutive stack operating hours, as defined in 40 CFR 72.2), in which to complete the required RATA for a particular CEMS whenever:

(1) A required RATA has not been performed by the end of the QA operating quarter in which it is due; or

## **Attachment: Mercury Monitoring Provisions**

(2) A required 3-load flow RATA has not been performed by the end of the calendar quarter in which it is due; or

(3) For a unit which is conditionally exempted under 40 CFR 75.21(a)(7) from the SO<sub>2</sub> RATA requirements of this attachment, an SO<sub>2</sub> RATA has not been completed by the end of the calendar quarter in which the annual usage of fuel(s) with a sulfur content higher than very low sulfur fuel (as defined in 40 CFR 72.2) exceeds 480 hours; or

(4) Eight successive calendar quarters have elapsed, following the quarter in which a RATA was last performed, without a subsequent RATA having been done, due either to infrequent operation of the unit(s) or frequent combustion of very low sulfur fuel, as defined in 40 CFR 72.2 (SO<sub>2</sub> monitors, only), or a combination of these factors.

(b) Except for SO<sub>2</sub> monitoring system RATAs, the grace period shall begin with the first unit (or stack) operating hour following the calendar quarter in which the required RATA was due. For SO<sub>2</sub> monitor RATAs, the grace period shall begin with the first unit (or stack) operating hour in which fuel with a total sulfur content higher than that of very low sulfur fuel (as defined in 40 CFR 72.2) is burned in the unit(s), following the quarter in which the required RATA is due. Data validation during a RATA grace period shall be done in accordance with the applicable provisions in section 2.3.2 of this appendix.

(c) If, at the end of the 720 unit (or stack) operating hour grace period, the RATA has not been completed, data from the monitoring system shall be invalid, beginning with the first unit operating hour following the expiration of the grace period. Data from the CEMS remain invalid until the hour of completion of a subsequent hands-off RATA. The deadline for the next test shall be either two QA operating quarters (if a semiannual RATA frequency is obtained) or four QA operating quarters (if an annual RATA frequency is obtained) after the quarter in which the RATA is completed, not to exceed eight calendar quarters.

(d) When a RATA is done during a grace period in order to satisfy a RATA requirement from a previous quarter, the deadline for the next RATA shall be determined as follows:

(1) If the grace period RATA qualifies for a reduced, (i.e., annual), RATA frequency the deadline for the next RATA shall be set at three QA operating quarters after the quarter in which the grace period test is completed.

(2) If the grace period RATA qualifies for the standard, (i.e., semiannual), RATA frequency the deadline for the next RATA shall be set at two QA operating quarters after the quarter in which the grace period test is completed.

(3) Notwithstanding these requirements, no more than eight successive calendar quarters shall elapse after the quarter in which the grace period test is completed, without a subsequent RATA having been conducted.



## **Attachment: Mercury Monitoring Provisions**

### **2.3.4 Bias Adjustment Factor**

Except as otherwise specified in section 7.6.5 of appendix A to this attachment, if an SO<sub>2</sub> pollutant concentration monitor, flow monitor, NO<sub>x</sub> CEMS, NO<sub>x</sub> concentration monitoring system used to calculate NO<sub>x</sub> mass emissions, Hg concentration monitoring system, or sorbent trap monitoring system fails the bias test specified in section 7.6 of appendix A to this attachment, use the bias adjustment factor given in Equations A-11 and A-12 of appendix A to this attachment, or the allowable alternative BAF specified in section 7.6.5(b) of appendix A to this attachment, to adjust the monitored data.

### **2.4 *Recertification, Quality Assurance, RATA Frequency and Bias Adjustment Factors (Special Considerations)***

(a) When a significant change is made to a monitoring system such that recertification of the monitoring system is required in accordance with 40 CFR 75.20(b), a recertification test (or tests) must be performed to ensure that the CEMS continues to generate valid data. In all recertifications, a RATA will be one of the required tests; for some recertifications, other tests will also be required. A recertification test may be used to satisfy the quality assurance test requirement of this appendix. For example, if, for a particular change made to a CEMS, one of the required recertification tests is a linearity check and the linearity check is successful, then, unless another such recertification event occurs in that same QA operating quarter, it would not be necessary to perform an additional linearity test of the CEMS in that quarter to meet the quality assurance requirement of section 2.2.1 of this appendix. For this reason, DEQ recommends that owners or operators coordinate component replacements, system upgrades, and other events that may require recertification, to the extent practicable, with the periodic quality assurance testing required by this appendix. When a quality assurance test is done for the dual purpose of recertification and routine quality assurance, the applicable data validation procedures in 40 CFR 75.20(b)(3) shall be followed.

(b) Except as provided in section 2.3.3 of this appendix, whenever a passing RATA of a gas monitor is performed, or a passing 2-load (or 2-level) RATA or a passing 3-load (or 3-level) RATA of a flow monitor is performed (irrespective of whether the RATA is done to satisfy a recertification requirement or to meet the quality assurance requirements of this appendix, or both), the RATA frequency (semi-annual or annual) shall be established based upon the date and time of completion of the RATA and the relative accuracy percentage obtained. For 2-load (or 2-level) and 3-load (or 3-level) flow RATAs, use the highest percentage relative accuracy at any of the loads (or levels) to determine the RATA frequency. The results of a single-load (or single-level) flow RATA may be used to establish the RATA frequency when the single-load (or single-level) flow RATA is specifically required under section 2.3.1.3(b) of this appendix or when the single-load (or single-level) RATA is allowed under section 2.3.1.3(c) of this appendix for a unit that has operated at one load level (or operating level) for  $\geq 85.0$  percent of the time since the last annual flow RATA. No other single-load (or single-level) flow RATA may be used to establish an annual RATA frequency; however, a 2-load or 3-load (or a 2-

## Attachment: Mercury Monitoring Provisions

level or 3-level) flow RATA may be performed at any time or in place of any required single-load (or single-level) RATA, in order to establish an annual RATA frequency.

### 2.5 Other Audits

Affected units may be subject to relative accuracy test audits at any time. If a monitor or continuous emission monitoring system fails the relative accuracy test during the audit, the monitor or continuous emission monitoring system shall be considered to be out-of-control beginning with the date and time of completion of the audit, and continuing until a successful audit test is completed following corrective action. If a monitor or monitoring system fails the bias test during an audit, use the bias adjustment factor given by equations A-11 and A-12 in appendix A to this attachment to adjust the monitored data. Apply this adjustment factor from the date and time of completion of the audit until the date and time of completion of a relative accuracy test audit that does not show bias.

### 2.6 System Integrity Checks for Hg Monitors

For each Hg concentration monitoring system (except for a Hg monitor that does not have a converter), perform a single-point system integrity check weekly, i.e., at least once every 168 unit or stack operating hours, using a NIST-traceable source of oxidized Hg. Perform this check using a mid- or high-level gas concentration, as defined in section 5.2 of appendix A to this attachment. The performance specifications in paragraph (3) of section 3.2 of appendix A to this attachment must be met, otherwise the monitoring system is considered out-of-control, from the hour of the failed check until a subsequent system integrity check is passed. If a required system integrity check is not performed and passed within 168 unit or stack operating hours of last successful check, the monitoring system shall also be considered out of control, beginning with the 169th unit or stack operating hour after the last successful check, and continuing until a subsequent system integrity check is passed. This weekly check is not required if the daily calibration assessments in section 2.1.1 of this appendix are performed using a NIST-traceable source of oxidized Hg.

**Figure 1 to Appendix B of Attachment.—Quality Assurance Test Requirements**

Test	Basic QA test frequency requirements*				
	Daily*	Weekly	Quarterly*	Semiannual*	Annual
Calibration Error Test (2 pt.)	Z				
Interference Check (flow)	Z				
Flow-to-Load Ratio			Z		
Leak Check (DP flow monitors)			Z		
Linearity Check or System Integrity Check** (3 pt.)			Z		

## Attachment: Mercury Monitoring Provisions

Test	Basic QA test frequency requirements*				
	Daily*	Weekly	Quarterly*	Semiannual*	Annual
Single-point System Integrity Check**		Z			
RATA (SO <sub>2</sub> , NO <sub>x</sub> , CO <sub>2</sub> , O <sub>2</sub> , H <sub>2</sub> O) <sup>1</sup>				Z	
RATA (All Hg monitoring systems)					Z
RATA (flow) <sup>12</sup>				Z	

\*“Daily” means operating days, only. “Weekly” means once every 168 unit or stack operating hours. “Quarterly” means once every QA operating quarter. “Semiannual” means once every two QA operating quarters. “Annual” means once every four QA operating quarters.

\*\*The system integrity check applies only to Hg monitors with converters. The single-point weekly system integrity check is not required if daily calibrations are performed using a NIST-traceable source of oxidized Hg. The 3-point quarterly system integrity check is not required if a linearity check is performed.

<sup>1</sup>Conduct RATA annually (i.e., once every four QA operating quarters), if monitor meets accuracy requirements to qualify for less frequent testing.

<sup>2</sup>For flow monitors installed on peaking units, bypass stacks, or units that qualify for single-level RATA testing under section 6.5.2(e) of this attachment, conduct all RATAs at a single, normal load (or operating level). For other flow monitors, conduct annual RATAs at two load levels (or operating levels). Alternating single-load and 2-load (or single-level and 2-level) RATAs may be done if a monitor is on a semiannual frequency. A single-load (or single-level) RATA may be done in lieu of a 2-load (or 2-level) RATA if, since the last annual flow RATA, the unit has operated at one load level (or operating level) for  $\geq 85.0$  percent of the time. A 3-level RATA is required at least once every five calendar years and whenever a flow monitor is re-linearized, except for flow monitors exempted from 3-level RATA testing under section 6.5.2(b) or 6.5.2(e) of appendix A to this attachment.

## Attachment: Mercury Monitoring Provisions

**Figure 2 to Appendix B of Attachment.—Relative Accuracy Test Frequency Incentive System**

RATA	Semiannual <sup>W</sup> (percent)	Annual <sup>W</sup>
SO <sub>2</sub> or NO <sub>x</sub> <sup>Y</sup>	7.5% < RA ≤ 10.0% or ±15.0 ppm <sup>X</sup>	RA ≤ 7.5% or ±12.0 ppm <sup>X</sup> .
SO <sub>2</sub> -diluent	7.5% < RA ≤ 10.0% or ±0.030 lb/mmBtu <sup>X</sup>	RA ≤ 7.5% or ±0.025 lb/mmBtu = G5X.
NO <sub>x</sub> -diluent	7.5% < RA ≤ 10.0% or ±0.020 lb/mmBtu <sup>X</sup>	RA ≤ 7.5% or ±0.015 lb/mmBtu <sup>X</sup> .
Flow	7.5% < RA ≤ 10.0% or ±2.0 fps <sup>X</sup>	RA ≤ 7.5% or ±1.5 fps <sup>X</sup> .
CO <sub>2</sub> or O <sub>2</sub>	7.5% < RA ≤ 10.0% or ±1.0% CO <sub>2</sub> /O <sub>2</sub> <sup>X</sup>	RA ≤ 7.5% or ±0.7% CO <sub>2</sub> /O <sub>2</sub> <sup>X</sup> .
Hg <sup>X</sup>	N/A	RA < 20.0% or ±1.0 µg/scm <sup>X</sup> .
Moisture	7.5% < RA ≤ 10.0% or ±1.5% H <sub>2</sub> O <sup>X</sup>	RA ≤ 7.5% or ±1.0% H <sub>2</sub> O <sup>X</sup> .

<sup>W</sup>The deadline for the next RATA is the end of the second (if semiannual) or fourth (if annual) successive QA operating quarter following the quarter in which the CEMS was last tested. Exclude calendar quarters with fewer than 168 unit operating hours (or, for common stacks and bypass stacks, exclude quarters with fewer than 168 stack operating hours) in determining the RATA deadline. For SO<sub>2</sub> monitors, QA operating quarters in which only very low sulfur fuel as defined in 40 CFR 72.2, is combusted may also be excluded. However, the exclusion of calendar quarters is limited as follows: the deadline for the next RATA shall be no more than 8 calendar quarters after the quarter in which a RATA was last performed.

<sup>X</sup>The difference between monitor and reference method mean values applies to moisture monitors, CO<sub>2</sub>, and O<sub>2</sub> monitors, low emitters of SO<sub>2</sub>, NO<sub>x</sub>, or Hg, or and low flow, only. The specifications for Hg monitors also apply to sorbent trap monitoring systems.

<sup>Y</sup>A NO<sub>x</sub> concentration monitoring system used to determine NO<sub>x</sub> mass emissions under 40 CFR 75.71.

## **Attachment: Mercury Monitoring Provisions**

### **Appendix C to Attachment.—Missing Data Estimation Procedures**

#### **1. Parametric Monitoring Procedure for Missing SO<sub>2</sub> Concentration or NO<sub>x</sub> Emission Rate Data**

##### *1.1 Applicability*

The permittee of any affected unit equipped with post-combustion SO<sub>2</sub> or NO<sub>x</sub> emission controls and SO<sub>2</sub> pollutant concentration monitors and/or NO<sub>x</sub> continuous emission monitoring systems at the inlet and outlet of the emission control system may apply to the DEQ for approval and certification of a parametric, empirical, or process simulation method or model for calculating substitute data for missing data periods. Such methods may be used to parametrically estimate the removal efficiency of the SO<sub>2</sub> of postcombustion NO<sub>x</sub> emission controls which, with the monitored inlet concentration or emission rate data, may be used to estimate the average concentration of SO<sub>2</sub> emissions or average emission rate of NO<sub>x</sub> discharged to the atmosphere. After approval by the DEQ, such method or model may be used for filling in missing SO<sub>2</sub> concentration or NO<sub>x</sub> emission rate data when data from the outlet SO<sub>2</sub> pollutant concentration monitor or outlet NO<sub>x</sub> continuous emission monitoring system have been reported with an annual monitor data availability of 90.0 percent or more.

Base the empirical and process simulation methods or models on the fundamental chemistry and engineering principles involved in the treatment of pollutant gas. On a case-by-case basis, the DEQ may pre-certify commercially available process simulation methods and models.

##### *1.2 Petition Requirements*

Continuously monitor, determine, and record hourly averages of the estimated SO<sub>2</sub> or NO<sub>x</sub> removal efficiency and of the parameters specified below, at a minimum. The affected facility shall supply additional parametric information where appropriate. Measure the SO<sub>2</sub> concentration or NO<sub>x</sub> emission rate, removal efficiency of the add-on emission controls, and the parameters for at least 2160 unit operating hours. Provide information for all expected operating conditions and removal efficiencies. At least 4 evenly spaced data points are required for a valid hourly average, except during periods of calibration, maintenance, or quality assurance activities, during which 2 data points per hour are sufficient. The DEQ will review all applications on a case-by-case basis.

##### **1.2.1 Parameters for Wet Flue Gas Desulfurization System**

**1.2.1.1** Number of scrubber modules in operation.

**1.2.1.2** Total slurry rate to each scrubber module (gal per min).

**1.2.1.3** In-line absorber pH of each scrubber module.

## **Attachment: Mercury Monitoring Provisions**

1.2.1.4 Pressure differential across each scrubber module (inches of water column).

1.2.1.5 Unit load (MWe).

1.2.1.6 Inlet and outlet SO<sub>2</sub> concentration as determined by the monitor or missing data substitution procedures.

1.2.1.7 Percent solids in slurry for each scrubber module.

1.2.1.8 Any other parameters necessary to verify scrubber removal efficiency, if the DEQ determines the parameters above are not sufficient.

### **1.2.2 Parameters for Dry Flue Gas Desulfurization System**

1.2.2.1 Number of scrubber modules in operation.

1.2.2.2 Atomizer slurry flow rate to each scrubber module (gal per min).

1.2.2.3 Inlet and outlet temperature for each scrubber module ( °F).

1.2.2.4 Pressure differential across each scrubber module (inches of water column).

1.2.2.5 Unit load (MWe).

1.2.2.6 Inlet and outlet SO<sub>2</sub> concentration as determined by the monitor or missing data substitution procedures.

1.2.2.7 Any other parameters necessary to verify scrubber removal efficiency, if the DEQ determines the parameters above are not sufficient.

### **1.2.4 Parameters for Post-Combustion NO<sub>x</sub> Emission Controls**

1.2.4.1 Inlet air flow rate to the unit (boiler) (mcf/hr).

1.2.4.2 Excess oxygen concentration of flue gas at stack outlet (percent).

1.2.4.3 Carbon monoxide concentration of flue gas at stack outlet (ppm).

1.2.4.4 Temperature of flue gas at outlet of the unit ( °F).

1.2.4.5 Inlet and outlet NO<sub>x</sub> emission rate as determined by the NO<sub>x</sub> continuous emission monitoring system or missing data substitution procedures.

1.2.4.6 Any other parameters specific to the emission reduction process necessary to verify the NO<sub>x</sub> control removal efficiency, (e.g., reagent feedrate in gal/mi).

## Attachment: Mercury Monitoring Provisions

### *1.3 Correlation of Emissions With Parameters*

Establish a method for correlating hourly averages of the parameters identified above with the percent removal efficiency of the SO<sub>2</sub> or post-combustion NO<sub>x</sub> emission controls under varying unit operating loads. Equations 1–7 in 40 CFR 75.15 may be used to estimate the percent removal efficiency of the SO<sub>2</sub> emission controls on an hourly basis.

Each parametric data substitution procedure should develop a data correlation procedure to verify the performance of the SO<sub>2</sub> emission controls or post-combustion NO<sub>x</sub> emission controls, along with the SO<sub>2</sub> pollutant concentration monitor and NO<sub>x</sub> continuous emission monitoring system values for varying unit load ranges.

For NO<sub>x</sub> emission rate data, and wherever the performance of the emission controls varies with the load, use the load range procedure provided in section 2.2 of this appendix.

### *1.4 Calculations*

1.4.1 Use the following equation to calculate substitute data for filling in missing (outlet) SO<sub>2</sub> pollutant concentration monitor data.

$$M_o = I_c(1-E)$$

(Eq. C-1)

where,

M<sub>o</sub> = Substitute data for outlet SO<sub>2</sub> concentration, ppm.

I<sub>c</sub> = Recorded inlet SO<sub>2</sub> concentration, ppm.

E = Removal efficiency of SO<sub>2</sub> emission controls as determined by the correlation procedure described in section 1.3 of this appendix.

1.4.2 Use the following equation to calculate substitute data for filling in missing (outlet) NO<sub>x</sub> emission rate data.

$$M_o = I_c(1-E)$$

(Eq. C-2)

where,

M<sub>o</sub> = Substitute data for outlet NO<sub>x</sub> emission rate, lb/mmBtu.

I<sub>c</sub> = Recorded inlet NO<sub>x</sub> emission rate, lb/mmBtu.

## **Attachment: Mercury Monitoring Provisions**

E = Removal efficiency of post-combustion NO<sub>x</sub> emission controls determined by the correlation procedure described in section 1.3 of this appendix.

### *1.5 Missing Data*

1.5.1 If both the inlet and the outlet SO<sub>2</sub> pollutant concentration monitors are unavailable simultaneously, use the maximum inlet SO<sub>2</sub> concentration recorded by the inlet SO<sub>2</sub> pollutant concentration monitor during the previous 720 quality-assured monitor operating hours to substitute for the inlet SO<sub>2</sub> concentration in equation C-1 of this appendix.

1.5.2 If both the inlet and outlet NO<sub>x</sub> continuous emission monitoring systems are unavailable simultaneously, use the maximum inlet NO<sub>x</sub> emission rate for the corresponding unit load recorded by the NO<sub>x</sub> continuous emission monitoring system at the inlet during the previous 2160 quality-assured monitor operating hours to substitute for the inlet NO<sub>x</sub> emission rate in equation C-2 of this appendix.

### *1.6 Application*

Apply to the DEQ for approval and certification of the parametric substitution procedure for filling in missing SO<sub>2</sub> concentration or NO<sub>x</sub> emission rate data using the established criteria and information identified above. Do not use this procedure until approved by the DEQ.

## **2. Load-based Procedure for Missing Flow Rate, NO<sub>x</sub> Concentration, and NO<sub>x</sub> Emission Rate Data**

### *2.1 Applicability*

This procedure is applicable for data from the CFB boiler for use in accordance with the provisions of this attachment to provide substitute data for volumetric flow rate (scfh), NO<sub>x</sub> emission rate (in lb/mmBtu) from NO<sub>x</sub>-diluent continuous emission monitoring systems, and NO<sub>x</sub> concentration data (in ppm) from NO<sub>x</sub> concentration monitoring systems used to determine NO<sub>x</sub> mass emissions.

### *2.2 Procedure*

2.2.1 For a single unit, establish ten operating load ranges defined in terms of percent of the maximum hourly average gross load of the unit, in gross megawatts (MWge), as shown in Table C-1. (Do not use integrated hourly gross load in MW-hr.)



## Attachment: Mercury Monitoring Provisions

**Table C-1—Definition of Operating Load Ranges for Load-based Substitution Data Procedures**

Operating load range	Percent of maximum hourly gross load or maximum hourly gross steam load (percent)
1	0–10
2	>10–20
3	>20–30
4	>30–40
5	>40–50
6	>50–60
7	>60–70
8	>70–80
9	>80–90
10	>90

2.2.2 Beginning with the first hour of unit operation after installation and certification of the flow monitor or the NO<sub>x</sub>-diluent continuous emission monitoring system (or a NO<sub>x</sub> concentration monitoring system used to determine NO<sub>x</sub> mass emissions, as defined in 40 CFR 75.71(a)(2)), for each hour of unit operation record a number, 1 through 10, (or 1 through 20 for flow at common stacks) that identifies the operating load range corresponding to the integrated hourly gross load of the unit(s) recorded for each unit operating hour.

2.2.3 Beginning with the first hour of unit operation after installation and certification of the flow monitor or the NO<sub>x</sub>-diluent continuous emission monitoring system (or a NO<sub>x</sub> concentration monitoring system used to determine NO<sub>x</sub> mass emissions, as defined in 40 CFR 75.71(a)(2)) and continuing thereafter, the data acquisition and handling system must be capable of calculating and recording the following information for each unit operating hour of missing flow or NO<sub>x</sub> data within each identified load range during the shorter of: (a) the previous 2,160 quality-assured monitor operating hours (on a rolling basis), or (b) all previous quality-assured monitor operating hours.

2.2.3.1 Average of the hourly flow rates reported by a flow monitor, in scfh.

2.2.3.2 The 90th percentile value of hourly flow rates, in scfh.

2.2.3.3 The 95th percentile value of hourly flow rates, in scfh.

2.2.3.4 The maximum value of hourly flow rates, in scfh.

## **Attachment: Mercury Monitoring Provisions**

2.2.3.5 Average of the hourly NO<sub>x</sub> emission rate, in lb/mmBtu, reported by a NO<sub>x</sub> continuous emission monitoring system.

2.2.3.6 The 90th percentile value of hourly NO<sub>x</sub> emission rates, in lb/mmBtu.

2.2.3.7 The 95th percentile value of hourly NO<sub>x</sub> emission rates, in lb/mmBtu.

2.2.3.8 The maximum value of hourly NO<sub>x</sub> emission rates, in lb/mmBtu.

2.2.3.9 Average of the hourly NO<sub>x</sub> pollutant concentrations, in ppm, reported by a NO<sub>x</sub> concentration monitoring system used to determine NO<sub>x</sub> mass emissions, as defined in 40 CFR 75.71(a)(2).

2.2.3.10 The 90th percentile value of hourly NO<sub>x</sub> pollutant concentration, in ppm.

2.2.3.11 The 95th percentile value of hourly NO<sub>x</sub> pollutant concentration, in ppm.

2.2.3.12 The maximum value of hourly NO<sub>x</sub> pollutant concentration, in ppm.

2.2.4 Calculate all monitor or continuous emission monitoring system data averages, maximum values, and percentile values determined by this procedure using bias adjusted values in the load ranges.

2.2.5 When a bias adjustment is necessary for the flow monitor and/or the NO<sub>x</sub>-diluent continuous emission monitoring system (and/or the NO<sub>x</sub> concentration monitoring system used to determine NO<sub>x</sub> mass emissions, as defined in 40 CFR 75.71(a)(2)), apply the adjustment factor to all monitor or continuous emission monitoring system data values placed in the load ranges.

2.2.6 Use the calculated monitor or monitoring system data averages, maximum values, and percentile values to substitute for missing flow rate and NO<sub>x</sub> emission rate data (and where applicable, NO<sub>x</sub> concentration data) according to the procedures in 40 CFR 75 subpart D.

## Attachment: Mercury Monitoring Provisions

### Appendix D to Attachment—Reserved

### Appendix E to Attachment—Reserved

### Appendix F to Attachment—Conversion Procedures

#### 1. Applicability

Use the procedures in this appendix to convert measured data from a monitor or continuous emission monitoring system into the appropriate units of the standard.

#### 2. Procedures for SO<sub>2</sub> Emissions

Use the following procedures to compute hourly SO<sub>2</sub> mass emission rate (in lb/hr) and quarterly and annual SO<sub>2</sub> total mass emissions (in tons).

2.1 When measurements of SO<sub>2</sub> concentration and flow rate are on a wet basis, use the following equation to compute hourly SO<sub>2</sub> mass emission rate (in lb/hr):

$$E_h = K C_h Q_h \quad (\text{Eq. F-1})$$

Where:

$E_h$  = Hourly SO<sub>2</sub> mass emission rate during unit operation, lb/hr.

$K = 1.660 \times 10^{-7}$  for SO<sub>2</sub>, (lb/scf)/ppm.

$C_h$  = Hourly average SO<sub>2</sub> concentration during unit operation, stack moisture basis, ppm.

$Q_h$  = Hourly average volumetric flow rate during unit operation, stack moisture basis, scfh.

2.2 When measurements by the SO<sub>2</sub> pollutant concentration monitor are on a dry basis and the flow rate monitor measurements are on a wet basis, use the following equation to compute hourly SO<sub>2</sub> mass emission rate (in lb/hr):

$$E_h = K C_{hp} Q_{hw} \frac{(100 - \%H_2O)}{100} \quad (\text{Eq. F-2})$$

where:

$E_h$  = Hourly SO<sub>2</sub> mass emission rate during unit operation, lb/hr.

$K = 1.660 \times 10^{-7}$  for SO<sub>2</sub>, (lb/scf)/ppm.

$C_{hp}$  = Hourly average SO<sub>2</sub> concentration during unit operation, ppm (dry).

## Attachment: Mercury Monitoring Provisions

$Q_{hs}$  = Hourly average volumetric flow rate during unit operation, scfh as measured (wet).

$\%H_2O$  = Hourly average stack moisture content during unit operation, percent by volume.

2.3 Use the following equations to calculate total  $SO_2$  mass emissions for each calendar quarter (Equation F-3) and for each calendar year (Equation F-4), in tons:

$$E_q = \frac{\sum_{k=1}^n E_k t_k}{2000}$$

(Eq. F-3)

Where:

$E_q$  = Quarterly total  $SO_2$  mass emissions, tons.

$E_h$  = Hourly  $SO_2$  mass emission rate, lb/hr.

$t_h$  = Unit operating time, hour or fraction of an hour (in equal increments that can range from one hundredth to one quarter of an hour, at the option of the permittee).

$n$  = Number of hourly  $SO_2$  emissions values during calendar quarter.

2000 = Conversion of 2000 lb per ton.

$$E_a = \sum_{q=1}^4 E_q \quad (\text{Eq. F-4})$$

Where:

$E_a$  = Annual total  $SO_2$  mass emissions, tons.

$E_q$  = Quarterly  $SO_2$  mass emissions, tons.

$q$  = Quarters for which  $E_q$  are available during calendar year.

2.4 Round all  $SO_2$  mass emission rates and totals to the nearest tenth.

### 3. Procedures for $NO_x$ Emission Rate

Use the following procedures to convert continuous emission monitoring system measurements of  $NO_x$  concentration (ppm) and diluent concentration (percentage) into  $NO_x$  emission rates (in lb/mmBtu). Perform measurements of  $NO_x$  and diluent ( $O_2$  or  $CO_2$ ) concentrations on the same moisture (wet or dry) basis.

## Attachment: Mercury Monitoring Provisions

3.1 When the NO<sub>x</sub> continuous emission monitoring system uses O<sub>2</sub> as the diluent, and measurements are performed on a dry basis, use the following conversion procedure:

$$E = K C_h F \frac{20.9}{20.9 - \%O_2}$$

(Eq. F-5)

where,

K, E, C<sub>h</sub>, F, and %O<sub>2</sub> are defined in section 3.3 of this appendix. When measurements are performed on a wet basis, use the equations in Method 19 in appendix A-7 to part 60 of this chapter.

3.2 When the NO<sub>x</sub> continuous emission monitoring system uses CO<sub>2</sub> as the diluent, use the following conversion procedure:

$$E = K C_h F_c \frac{100}{\%CO_2}$$

(Eq. F-6)

where:

K, E, C<sub>h</sub>, F<sub>c</sub>, and %CO<sub>2</sub> are defined in section 3.3 of this appendix.

When CO<sub>2</sub> and NO<sub>x</sub> measurements are performed on a different moisture basis, use the equations in Method 19 in appendix A-7 to part 60 of this chapter.

3.3 Use the definitions listed below to derive values for the parameters in equations F-5 and F-6 of this appendix, or (if applicable) in the equations in Method 19 in appendix A-7 to part 60 of this chapter.

3.3.1  $K = 1.194 \times 10^{-7} (\text{lb/dscf})/\text{ppm NO}_x$ .

3.3.2 E = Pollutant emissions during unit operation, lb/mmBtu.

3.3.3 C<sub>h</sub> = Hourly average pollutant concentration during unit operation, ppm.

3.3.4 %O<sub>2</sub>, %CO<sub>2</sub> = Oxygen or carbon dioxide volume during unit operation (expressed as percent O<sub>2</sub> or CO<sub>2</sub>).

3.3.4.1 For boilers, a minimum concentration of 5.0 percent CO<sub>2</sub> or a maximum concentration of 14.0 percent O<sub>2</sub> may be substituted for the measured diluent gas concentration value for any operating hour in which the hourly average CO<sub>2</sub>

## Attachment: Mercury Monitoring Provisions

concentration is < 5.0 percent CO<sub>2</sub> or the hourly average O<sub>2</sub> concentration is > 14.0 percent O<sub>2</sub>

3.3.4.2 If NO<sub>x</sub> emission rate is calculated using either Equation 19–3 or 19–5 in Method 19 in appendix A–7 to 40 CFR part 60, a variant of the equation shall be used whenever the diluent cap is applied. The modified equations shall be designated as Equations 19–3D and 19–5D, respectively. Equation 19–3D is structurally the same as Equation 19–3, except that the term “%O<sub>2</sub>w” in the denominator is replaced with the term “%O<sub>2</sub>dc × [(100–% H<sub>2</sub>O)/100]”, where %O<sub>2</sub>dc is the diluent cap value. The numerator of Equation 19–5D is the same as Equation 19–5; however, the denominator of Equation 19–5D is simply “20.9–%O<sub>2</sub>dc”, where %O<sub>2</sub>dc is the diluent cap value.

3.3.5 F, F<sub>c</sub>=a factor representing a ratio of the volume of dry flue gases generated to the caloric value of the fuel combusted (F), and a factor representing a ratio of the volume of CO<sub>2</sub> generated to the calorific value of the fuel combusted (F<sub>c</sub>), respectively. Table 1 lists the values of F and F<sub>c</sub> for different fuels.

**Table 1.—F- and F<sub>c</sub>-Factors<sup>1</sup>**

<b>Fuel</b>	<b>F-factor (dscf/mmBtu)</b>	<b>F<sub>c</sub>-factor (scf CO<sub>2</sub>/mmBtu)</b>
Coal (as defined by ASTM D388–99 <sup>2</sup> ):		
Anthracite	10,100	1,970
Bituminous	9,780	1,800
Subbituminous	9,820	1,840
Lignite	9,860	1,910
Petroleum Coke	9,830	1,850
Tire Derived Fuel	10,260	1,800
Oil	9,190	1,420
Gas:		
Natural gas	8,710	1,040
Propane	8,710	1,190
Butane	8,710	1,250
Wood:		
Bark	9,600	1,920
Wood residue	9,240	1,830

## Attachment: Mercury Monitoring Provisions

<sup>1</sup>Determined at standard conditions: 20 °C (68 °F) and 29.92 inches of mercury.

<sup>2</sup>Incorporated by reference under 40 CFR 75.6.

3.3.6 Equations F-7a and F-7b may be used in lieu of the F or F<sub>c</sub> factors specified in Section 3.3.5 of this appendix to calculate a site-specific dry-basis F factor (dscf/mmBtu) or a site-specific F<sub>c</sub> factor (scf CO<sub>2</sub>/mmBtu), on either a dry or wet basis. At a minimum, the site-specific F or F<sub>c</sub> factor must be based on 9 samples of the fuel. Fuel samples taken during each run of a RATA are acceptable for this purpose. The site-specific F or F<sub>c</sub> factor must be re-determined at least annually, and the value from the most recent determination must be used in the emission calculations. Alternatively, the previous F or F<sub>c</sub> value may continue to be used if it is higher than the value obtained in the most recent determination. The permittee shall keep records of all site-specific F or F<sub>c</sub> determinations, active for at least 3 years. (Calculate all F- and F<sub>c</sub> factors at standard conditions of 20 °C (68 °F) and 29.92 inches of mercury).

$$F = \frac{3.64 (\%H) + 1.53 (\%C) + 0.57 (\%S) + 0.14 (\%N) - 0.46 (\%O)}{GCV} \times 10^6$$

(Eq. F-7a)

$$F_c = \frac{321 \times 10^3 (\%C)}{GCV}$$

(Eq. F-7b)

3.3.6.1 H, C, S, N, and O are content by weight of hydrogen, carbon, sulfur, nitrogen, and oxygen (expressed as percent), respectively, as determined on the same basis as the gross calorific value (GCV) by ultimate analysis of the fuel combusted using ASTM D3176-89 (Reapproved 2002), Standard Practice for Ultimate Analysis of Coal and Coke, (solid fuels), ASTM D5291-02, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants, (liquid fuels) or computed from results using ASTM D1945-96 (Reapproved 2001), Standard Test Method for Analysis of Natural Gas by Gas Chromatography, or ASTM D1946-90 (Reapproved 2006), Standard Practice for Analysis of Reformed Gas by Gas Chromatography, (gaseous fuels) as applicable. (All of these methods are incorporated by reference under 40 CFR 75.6.)

3.3.6.2 GCV is the gross calorific value (Btu/lb) of the fuel combusted determined by ASTM D5865-01a, Standard Test Method for Gross Calorific Value of Coal and Coke, and ASTM D240-00, Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter, or ASTM D4809-00, Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method) for oil; and ASTM D3588-98, Standard Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels, ASTM D4891-89 (Reapproved 2006), Standard Test Method for Heating Value of Gases in Natural Gas Range by Stoichiometric Combustion, GPA Standard 2172-96 Calculation of Gross

## Attachment: Mercury Monitoring Provisions

Heating Value, Relative Density and Compressibility Factor for Natural Gas Mixtures from Compositional Analysis, GPA Standard 2261-00 Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography, or ASTM D1826-94 (Reapproved 1998), Standard Test Method for Calorific (Heating) Value of Gases in Natural Gas Range by Continuous Recording Calorimeter, for gaseous fuels, as applicable. (All of these methods are incorporated by reference under 40 CFR 75.6).

3.3.6.3 For affected units that combust a combination of a fuel (or fuels) listed in Table 1 in section 3.3.5 of this appendix with any fuel(s) not listed in Table 1, the F or F<sub>c</sub> value is subject to the DEQ's approval under 40 CFR 75.66.

3.3.6.4 For affected units that combust combinations of fuels listed in Table 1 in section 3.3.5 of this appendix, prorate the F or F<sub>c</sub> factors determined by section 3.3.5 or 3.3.6 of this appendix in accordance with the applicable formula as follows:

$$F = \sum_{i=1}^n X_i F_i \quad F_c = \sum_{i=1}^n X_i (F_{c,i})$$

Where,

X<sub>i</sub> = Fraction of total heat input derived from each type of fuel (e.g., natural gas, bituminous coal, wood). Each X<sub>i</sub> value shall be determined from the best available information on the quantity of fuel combusted and the GCV value, over a specified time period. The permittee shall explain the method used to calculate X<sub>i</sub> in the hardcopy portion of the monitoring plan for the unit. The X<sub>i</sub> values may be determined and updated either hourly, daily, weekly, or monthly. In all cases, the prorated F-factor used in the emission calculations shall be determined using the X<sub>i</sub> values from the most recent update.

F<sub>i</sub> or (F<sub>c</sub>)<sub>i</sub> = Applicable F or F<sub>c</sub> factor for each fuel type determined in accordance with Section 3.3.5 or 3.3.6 of this appendix.

n = Number of fuels being combusted in combination.

3.3.6.5 As an alternative to prorating the F or F<sub>c</sub> factor as described in section 3.3.6.4 of this appendix, a "worst-case" F or F<sub>c</sub> factor may be reported for any unit operating hour. The worst-case F or F<sub>c</sub> factor shall be the highest F or F<sub>c</sub> value for any of the fuels combusted in the unit.

3.4 Use the following equations to calculate the average NO<sub>x</sub> emission rate for each calendar quarter (Equation F-9) and the average emission rate for the calendar year (Equation F-10), in lb/mmBtu:

$$E_{q_i} = \sum_{j=1}^n \frac{E_{q_{ij}}}{n} \quad (\text{Eq. F-9})$$



## Attachment: Mercury Monitoring Provisions

Where:

$E_q$  = Quarterly average  $\text{NO}_x$  emission rate, lb/mmBtu.

$E_i$  = Hourly average  $\text{NO}_x$  emission rate during unit operation, lb/mmBtu.

$n$  = Number of hourly rates during calendar quarter.

$$E_q = \sum_{i=1}^n \frac{E_i}{m} \quad (\text{Eq. F-10})$$

Where:

$E_a$  = Average  $\text{NO}_x$  emission rate for the calendar year, lb/mmBtu.

$E_i$  = Hourly average  $\text{NO}_x$  emission rate during unit operation, lb/mmBtu.

$m$  = Number of hourly rates for which  $E_i$  is available in the calendar year.

3.5 Round all  $\text{NO}_x$  emission rates to the nearest 0.001 lb/mmBtu.

### 4. Procedures for $\text{CO}_2$ Mass Emissions

Use the following procedures to convert continuous emission monitoring system measurements of  $\text{CO}_2$  concentration (percentage) and volumetric flow rate (scfh) into  $\text{CO}_2$  mass emissions (in tons/day) when the permittee uses a  $\text{CO}_2$  continuous emission monitoring system (consisting of a  $\text{CO}_2$  or  $\text{O}_2$  pollutant monitor) and a flow monitoring system to monitor  $\text{CO}_2$  emissions from an affected unit.

4.1 When  $\text{CO}_2$  concentration is measured on a wet basis, use the following equation to calculate hourly  $\text{CO}_2$  mass emissions rates (in tons/hr):

$$E_h = KC_hQ_h \quad (\text{Eq. F-11})$$

Where:

$E_h$  = Hourly  $\text{CO}_2$  mass emission rate during unit operation, tons/hr.

$K = 5.7 \times 10^{-7}$  for  $\text{CO}_2$ , (tons/scf) / % $\text{CO}_2$ .

$C_h$  = Hourly average  $\text{CO}_2$  concentration during unit operation, wet basis, either measured directly with a  $\text{CO}_2$  monitor or calculated from wet-basis  $\text{O}_2$  data using Equation F-14b, percent  $\text{CO}_2$ .

$Q_h$  = Hourly average volumetric flow rate during unit operation, wet basis, scfh.

## Attachment: Mercury Monitoring Provisions

4.2 When CO<sub>2</sub> concentration is measured on a dry basis, use Equation F-2 to calculate the hourly CO<sub>2</sub> mass emission rate (in tons/hr) with a K-value of  $5.7 \times 10^{-7}$  (tons/scf) percent CO<sub>2</sub>, where E<sub>h</sub>= hourly CO<sub>2</sub> mass emission rate, tons/hr and C<sub>hp</sub>= hourly average CO<sub>2</sub> concentration in flue, dry basis, percent CO<sub>2</sub>.

4.3 Use the following equations to calculate total CO<sub>2</sub> mass emissions for each calendar quarter (Equation F-12) and for each calendar year (Equation F-13):

$$E_{CO_2q} = \sum_{n=1}^{H_R} E_h t_h \quad (\text{Eq. F-12})$$

Where:

E<sub>CO<sub>2</sub>q</sub>= Quarterly total CO<sub>2</sub> mass emissions, tons.

E<sub>h</sub>= Hourly CO<sub>2</sub> mass emission rate, tons/hr.

t<sub>h</sub>=Unit operating time, in hours or fraction of an hour (in equal increments that can range from one hundredth to one quarter of an hour, at the option of the permittee).

H<sub>R</sub>= Number of hourly CO<sub>2</sub> mass emission rates available during calendar quarter.

$$E_{CO_2a} = \sum_{q=1}^4 E_{CO_2q} \quad (\text{Eq. F-13})$$

Where:

E<sub>CO<sub>2</sub>a</sub>= Annual total CO<sub>2</sub> mass emissions, tons.

E<sub>CO<sub>2</sub>q</sub>= Quarterly total CO<sub>2</sub> mass emissions, tons.

q = Quarters for which E<sub>CO<sub>2</sub>q</sub> are available during calendar year.

4.4 For each CFB boiler, when permittee is continuously monitoring O<sub>2</sub> concentration (in percent by volume) of flue gases using an O<sub>2</sub> monitor, use the equations and procedures in section 4.4.1 and 4.4.2 of this appendix to determine hourly CO<sub>2</sub> mass emissions (in tons).

4.4.1 If the permittee elects to use data from an O<sub>2</sub> monitor to calculate CO<sub>2</sub> concentration, the appropriate F and F<sub>C</sub> factors from section 3.3.5 of this appendix shall be used in one of the following equations (as applicable) to determine hourly average CO<sub>2</sub> concentration of flue gases (in percent by volume) from the measured hourly average O<sub>2</sub> concentration:

$$CO_{2d} = 100 \frac{F_c}{F} \frac{20.9 - O_{2d}}{20.9} \quad (\text{Eq. F-14a})$$

## Attachment: Mercury Monitoring Provisions

Where:

CO<sub>2d</sub> = Hourly average CO<sub>2</sub> concentration during unit operation, percent by volume, dry basis.

F, F<sub>C</sub> = F-factor or carbon-based F<sub>C</sub>-factor from section 3.3.5 of this appendix.

20.9 = Percentage of O<sub>2</sub> in ambient air.

O<sub>2d</sub> = Hourly average O<sub>2</sub> concentration during unit operation, percent by volume, dry basis.

$$CO_{2w} = \frac{100 F_c}{20.9 F} \left[ 20.9 \left( \frac{100 - \%H_2O}{100} \right) - O_{2w} \right] \quad (\text{Eq. F-14b})$$

Where:

CO<sub>2w</sub> = Hourly average CO<sub>2</sub> concentration during unit operation, percent by volume, wet basis.

O<sub>2w</sub> = Hourly average O<sub>2</sub> concentration during unit operation, percent by volume, wet basis.

F, F<sub>C</sub> = F-factor or carbon-based FC-factor from section 3.3.5 of this appendix.

20.9 = Percentage of O<sub>2</sub> in ambient air.

%H<sub>2</sub>O = Moisture content of gas in the stack, percent.

For any hour where Equation F-14a or F-14b results in a negative hourly average CO<sub>2</sub> value, 0.0% CO<sub>2w</sub> shall be recorded as the average CO<sub>2</sub> value for that hour.

4.4.2 Determine CO<sub>2</sub> mass emissions (in tons) from hourly average CO<sub>2</sub> concentration (percent by volume) using equation F-11 and the procedure in section 4.1, where O<sub>2</sub> measurements are on a wet basis, or using the procedures in section 4.2 of this appendix, where O<sub>2</sub> measurements are on a dry basis.

### 5. Procedures for Heat Input

Use the following procedures to compute heat input rate to an affected unit (in mmBtu/hr or mmBtu/day):

5.1 Calculate and record heat input rate to an affected unit on an hourly basis, except as provided in sections 5.5 through 5.5.7. The permittee may choose to use the provisions specified in 40 CFR 75.16(e) or in section 2.1.2 of appendix D to this attachment in

## Attachment: Mercury Monitoring Provisions

conjunction with the procedures provided in sections 5.6 through 5.6.2 to apportion heat input among each unit using the common stack or common pipe header.

5.2 For an affected unit that has a flow monitor (or approved alternate monitoring system under 40 CFR 75 subpart E for measuring volumetric flow rate) and a diluent gas (O<sub>2</sub> or CO<sub>2</sub>) monitor, use the recorded data from these monitors and one of the following equations to calculate hourly heat input rate (in mmBtu/hr).

5.2.1 When measurements of CO<sub>2</sub> concentration are on a wet basis, use the following equation:

$$HI = Q_w \frac{1}{F_c} \frac{\%CO_{2w}}{100} \quad (Eq. F-15)$$

Where:

HI = Hourly heat input rate during unit operation, mmBtu/hr.

Q<sub>w</sub> = Hourly average volumetric flow rate during unit operation, wet basis, scfh.

F<sub>c</sub> = Carbon-based F-factor, listed in section 3.3.5 of this appendix for each fuel, scf/mmBtu.

%CO<sub>2w</sub> = Hourly concentration of CO<sub>2</sub> during unit operation, percent CO<sub>2</sub> wet basis.

5.2.2 When measurements of CO<sub>2</sub> concentration are on a dry basis, use the following equation:

$$HI = Q_h \left[ \frac{(100 - \%H_2O)}{100 F_c} \right] \left( \frac{\%CO_{2d}}{100} \right) \quad (Eq. F-16)$$

Where:

HI = Hourly heat input rate during unit operation, mmBtu/hr.

Q<sub>h</sub> = Hourly average volumetric flow rate during unit operation, wet basis, scfh.

F<sub>c</sub> = Carbon-based F-Factor, listed in section 3.3.5 of this appendix for each fuel, scf/mmBtu.

%CO<sub>2d</sub> = Hourly concentration of CO<sub>2</sub> during unit operation, percent CO<sub>2</sub> dry basis.

%H<sub>2</sub>O = Moisture content of gas in the stack, percent.

5.2.3 When measurements of O<sub>2</sub> concentration are on a wet basis, use the following equation:

## Attachment: Mercury Monitoring Provisions

$$HI = Q_w \frac{1}{F} \left[ \frac{(20.9/100)[(100 - \%H_2O) - \%O_{2w}]}{20.9} \right] \quad (Eq. F-17)$$

Where:

HI = Hourly heat input rate during unit operation, mmBtu/hr.

$Q_w$  = Hourly average volumetric flow rate during unit operation, wet basis, scfh.

F = Dry basis F-factor, listed in section 3.3.5 of this appendix for each fuel, dscf/mmBtu.

$\%O_{2w}$  = Hourly concentration of  $O_2$  during unit operation, percent  $O_2$  wet basis. For any operating hour where Equation F-17 results in an hourly heat input rate that is  $\leq 0.0$  mmBtu/hr, 1.0 mmBtu/hr shall be recorded and reported as the heat input rate for that hour.

$\%H_2O$  = Hourly average stack moisture content, percent by volume.

5.2.4 When measurements of  $O_2$  concentration are on a dry basis, use the following equation:

$$HI = Q_w \left[ \frac{(100 - \%H_2O)}{100 F} \right] \left[ \frac{(20.9 - \%O_{2d})}{20.9} \right] \quad (Eq. F-18)$$

Where:

HI = Hourly heat input rate during unit operation, mmBtu/hr.

$Q_w$  = Hourly average volumetric flow during unit operation, wet basis, scfh.

F = Dry basis F-factor, listed in section 3.3.5 of this appendix for each fuel, dscf/mmBtu.

$\%H_2O$  = Moisture content of the stack gas, percent.

$\%O_{2d}$  = Hourly concentration of  $O_2$  during unit operation, percent  $O_2$  dry basis.

### 5.3 Heat Input Summation (for Heat Input Determined Using a Flow Monitor and Diluent Monitor)

5.3.1 Calculate total quarterly heat input for each CFB boiler using a flow monitor and diluent monitor to calculate heat input, using the following equation:

$$HI_q = \sum_{i=1}^n HI_i \quad (Eq. F-18a)$$

## Attachment: Mercury Monitoring Provisions

Where:

$HI_q$  = Total heat input for the quarter, mmBtu.

$HI_i$  = Hourly heat input rate during unit operation, using Equation F-15, F-16, F-17, or F-18, mmBtu/hr.

$t_i$  = Hourly operating time for the unit, hour or fraction of an hour (in equal increments that can range from one hundredth to one quarter of an hour, at the option of the permittee).

5.3.2 Calculate total cumulative heat input for each CFB boiler using a flow monitor and diluent monitor to calculate heat input, using the following equation:

$$HI_c = \sum_{q=1}^{4} HI_q \quad (\text{Eq. F-18b})$$

Where:

$HI_c$  = Total heat input for the year to date, mmBtu.

$HI_q$  = Total heat input for the quarter, mmBtu.

### 5.4 [Reserved]

5.5. When the unit is combusting coal, use the procedures, methods, and equations in sections 5.5.3.1–5.5.3.3 of this appendix to determine the heat input from coal for each 24-hour period. (All ASTM methods are incorporated by reference under 40 CFR 75.6)

5.5.1 Perform coal sampling daily according to section 5.3.2.2 in Method 19 in appendix A to part 60 of this chapter and use ASTM D2234–00, Standard Practice for Collection of a Gross Sample of Coal, (incorporated by reference under 40 CFR 75.6) Type I, Conditions A, B, or C and systematic spacing for sampling. (When performing coal sampling solely for the purposes of the missing data procedures in 40 CFR 75.36, use of ASTM D2234–00 is optional, and coal samples may be taken weekly.)

5.5.2 All ASTM methods are incorporated by reference under 40 CFR 75.6. Use ASTM D2013–01, Standard Practice for Preparing Coal Samples for Analysis, for preparation of a daily coal sample and analyze each daily coal sample for gross calorific value using ASTM D5865–01a, Standard Test Method for Gross Calorific Value of Coal and Coke. On-line coal analysis may also be used if the on-line analytical instrument has been demonstrated to be equivalent to the applicable ASTM methods under 40 CFR 75.23 and 40 CFR 75.66.

## Attachment: Mercury Monitoring Provisions

5.5.3 Calculate the heat input from coal using the following equation:

$$HI_c = M_c \frac{GCV_c}{500} \quad (Eq. F-21)$$

(Eq. F-21)

where:

$HI_c$  = Daily heat input from coal, mmBtu/day.

$M_c$  = Mass of coal consumed per day, as measured and recorded in company records, tons.

$GCV_c$  = Gross calorific value of coal sample, as measured by ASTM D3176-89 (Reapproved 2002), or ASTM D5865-01a, Btu/lb. (incorporated by reference under 40 CFR 75.6).

500 = Conversion of Btu/lb to mmBtu/ton.

5.5.4 For units obtaining heat input values daily instead of hourly, apportion the daily heat input using the fraction of the daily steam load or daily unit operating load used each hour in order to obtain  $HI_i$  for use in the above equations. Alternatively, use the hourly mass of coal consumed in equation F-21.

5.5.5 If a daily fuel sampling value for gross calorific value is not available, substitute the maximum gross calorific value measured from the previous 30 daily samples. If a monthly fuel sampling value for gross calorific value is not available, substitute the maximum gross calorific value measured from the previous 3 monthly samples.

5.5.6 If a daily coal consumption value is not available, substitute the maximum fuel feed rate during the previous thirty days when the unit burned coal.

5.5.7 Results for samples must be available no later than thirty calendar days after the sample is composited or taken. However, during an audit, the DEQ may require that the results be available in five business days, or sooner if practicable.

## 6. Procedure for Converting Volumetric Flow to STP

Use the following equation to convert volumetric flow at actual temperature and pressure to standard temperature and pressure.

$$F_{STP} = F_{Actual} (T_{Std}/T_{Stack}) (P_{Stack}/P_{Std})$$

## Attachment: Mercury Monitoring Provisions

where:

$F_{STP}$  = Flue gas volumetric flow rate at standard temperature and pressure, scfh.

$F_{Actual}$  = Flue gas volumetric flow rate at actual temperature and pressure, acfh.

$T_{Std}$  = Standard temperature = 528 °R.

$T_{Stack}$  = Flue gas temperature at flow monitor location, °R, where °R = 460 + °F.

$P_{Stack}$  = The absolute flue gas pressure = barometric pressure at the flow monitor location + flue gas static pressure, inches of mercury.

$P_{Std}$  = Standard pressure = 29.92 inches of mercury.

### 7. Procedures for SO<sub>2</sub> Mass Emissions, Using Default SO<sub>2</sub> Emission Rates and Heat Input Measured by CEMS

Equation F-23 may be applied to the combustion of solid or liquid fuel that meets the definition of very low sulfur fuel in 40 CFR 72.2, combinations of such fuels, or mixtures of such fuels with gaseous fuel, if the permittee has received approval from the DEQ under 40 CFR 75.66 to use a site-specific default SO<sub>2</sub> emission rate for the fuel or mixture of fuels.

$$E_h = (ER)(HI) \quad (\text{Eq. F-23})$$

Where:

$E_h$  = Hourly SO<sub>2</sub> mass emission rate, lb/hr.

ER = Applicable SO<sub>2</sub> default emission rate for the combustion of very low sulfur liquid or solid fuel, combinations of such fuels, or mixtures of such fuels with gaseous fuel, as approved by the DEQ under 40 CFR 75.66, lb/mmBtu.

HI = Hourly heat input rate, determined using the procedures in section 5.2 of this appendix, mmBtu/hr.

### 8. Procedures for NO<sub>x</sub> Mass Emissions

The owner or operator of a unit that is required to monitor, record, and report NO<sub>x</sub> mass emissions under a State or federal NO<sub>x</sub> mass emission reduction program must use the procedures in section 8.1, 8.2, or 8.3 of this appendix, as applicable, to account for hourly NO<sub>x</sub> mass emissions, and the procedures in section 8.4 of this appendix to account for quarterly, seasonal, and annual NO<sub>x</sub> mass emissions to the extent that the provisions of subpart H of this attachment are adopted as requirements under such a program.



## Attachment: Mercury Monitoring Provisions

8.1 The owner or operator may use the hourly NO<sub>x</sub> emission rate and the hourly heat input rate to calculate the NO<sub>x</sub> mass emissions in pounds or the NO<sub>x</sub> mass emission rate in pounds per hour, (as required by the applicable reporting format), for each unit or stack operating hour, as follows:

8.1.1 If both NO<sub>x</sub> emission rate and heat input rate are monitored at the same unit or stack level (e.g., the NO<sub>x</sub> emission rate value and the heat input rate value both represent all of the units exhausting to the common stack), then (as required by the applicable reporting format) either:

(a) Use Equation F-24 to calculate the hourly NO<sub>x</sub> mass emissions (lb).

$$M_{(\text{NO}_x)_h} = ER_{(\text{NO}_x)_h} HI_h t_h \quad (\text{Eq. F-24})$$

Where:

$M(\text{NO}_x)_h$  = NO<sub>x</sub> mass emissions in lbs for the hour.

$ER(\text{NO}_x)_h$  = Hourly average NO<sub>x</sub> emission rate for hour h, lb/mmBtu, from section 3 of this appendix, from Method 19 in appendix A-7 to part 60 of this chapter, or from section 3.3 of appendix E to this part. (Include bias-adjusted NO<sub>x</sub> emission rate values, where the bias-test procedures in appendix A to this part shows a bias-adjustment factor is necessary.)

$HI_h$  = Hourly average heat input rate for hour h, mmBtu/hr. (Include bias-adjusted flow rate values, where the bias-test procedures in appendix A to this part shows a bias-adjustment factor is necessary.)

$t_h$  = Monitoring location operating time for hour h, in hours or fraction of an hour (in equal increments that can range from one hundredth to one quarter of an hour, at the option of the permittee). If the combined NO<sub>x</sub> emission rate and heat input are monitored for all of the units in a common stack, the monitoring location operating time is equal to the total time when any of those units was exhausting through the common stack; or

(b) Use Equation F-24a to calculate the hourly NO<sub>x</sub> mass emission rate (lb/hr).

$$E_{(\text{NO}_x)_h} = ER_{(\text{NO}_x)_h} HI_h \quad (\text{Eq. F-24a})$$

Where:

$E(\text{NO}_x)_h$  = NO<sub>x</sub> mass emissions rate in lbs/hr for the hour.

$ER(\text{NO}_x)_h$  = Hourly average NO<sub>x</sub> emission rate for hour h, lb/mmBtu, from section 3 of this appendix, from Method 19 in appendix A-7 to part 60 of this chapter, or from section 3.3 of appendix E to this part. (Include bias-adjusted NO<sub>x</sub> emission rate values, where the

## Attachment: Mercury Monitoring Provisions

bias-test procedures in appendix A to this part shows a bias-adjustment factor is necessary.)

$HI_h$  = Hourly average heat input rate for hour h, mmBtu/hr. (Include bias-adjusted flow rate values, where the bias-test procedures in appendix A to this part shows a bias-adjustment factor is necessary.)

8.2 Alternatively, the permittee may use the hourly  $NO_x$  concentration (as measured by a  $NO_x$  concentration monitoring system) and the hourly stack gas volumetric flow rate to calculate the  $NO_x$  mass emission rate (lb/hr) for each unit or stack operating hour, in accordance with section 8.2.1 or 8.2.2 of this appendix (as applicable). If the hourly  $NO_x$  mass emissions are to be reported in lb, Equation F-26c in section 8.3 of this appendix shall be used to convert the hourly  $NO_x$  mass emission rates to hourly  $NO_x$  mass emissions (lb).

8.2.1 When the  $NO_x$  concentration monitoring system measures on a wet basis, first calculate the hourly  $NO_x$  mass emission rate (in lb/hr) during unit (or stack) operation, using Equation F-26a. (Include bias-adjusted flow rate or  $NO_x$  concentration values, where the bias-test procedures in appendix A to this attachment shows a bias-adjustment factor is necessary.)

$$E_{(NO_x)_h} = K C_{hw} Q_h \quad (\text{Eq. F-26a})$$

Where:

$E(NO_x)_h$  =  $NO_x$  mass emissions rate in lb/hr.

$K = 1.194 \times 10^{-7}$  for  $NO_x$ , (lb/scf)/ppm.

$C_{hw}$  = Hourly average  $NO_x$  concentration during unit operation, wet basis, ppm.

$Q_h$  = Hourly average volumetric flow rate during unit operation, wet basis, scfh.

8.2.2 When  $NO_x$  mass emissions are determined using a dry basis  $NO_x$  concentration monitoring system and a wet basis flow monitoring system, first calculate hourly  $NO_x$  mass emission rate (in lb/hr) during unit (or stack) operation, using Equation F-26b. (Include bias-adjusted flow rate or  $NO_x$  concentration values, where the bias-test procedures in appendix A to this part shows a bias-adjustment factor is necessary.)

$$E_{(NO_x)_h} = K C_M Q_h \frac{(100 - \%H_2O)}{(100)} \quad (\text{Eq. F-26b})$$

Where:

## Attachment: Mercury Monitoring Provisions

$E(\text{NO}_X)_h$  =  $\text{NO}_X$  mass emissions rate, lb/hr.

$K = 1.194 \times 10^{-7}$  for  $\text{NO}_X$ , (lb/scf)/ppm.

$C_{hd}$  = Hourly average  $\text{NO}_X$  concentration during unit operation, dry basis, ppm.

$Q_h$  = Hourly average volumetric flow rate during unit operation, wet basis, scfh.

$\%\text{H}_2\text{O}$  = Hourly average stack moisture content during unit operation, percent by volume.

8.3 When hourly  $\text{NO}_X$  mass emissions are reported in pounds and are determined using a  $\text{NO}_X$  concentration monitoring system and a flow monitoring system, calculate  $\text{NO}_X$  mass emissions (lb) for each unit or stack operating hour by multiplying the hourly  $\text{NO}_X$  mass emission rate (lb/hr) by the unit operating time for the hour, as follows:

$$M_{(\text{NO}_X)_h} = E_h t_h \quad (\text{Eq. F-26c})$$

Where:

$M(\text{NO}_X)_h$  =  $\text{NO}_X$  mass emissions for the hour, lb.

$E_h$  = Hourly  $\text{NO}_X$  mass emission rate during unit (or stack) operation from Equation F-26a in section 8.2.1 of this appendix or Equation F-26b in section 8.2.2 of this appendix (as applicable), lb/hr.

$t_h$  = Unit operating time or stack operating time (as defined in 40 CFR 72.2) for hour "h", in hours or fraction of an hour (in equal increments that can range from one hundredth to one quarter of an hour, at the option of the permittee).

8.4 Use the following procedures to calculate quarterly, cumulative ozone season, and cumulative yearly  $\text{NO}_X$  mass emissions, in tons:

(a) When hourly  $\text{NO}_X$  mass emissions are reported in lb., use Eq. F-27.

$$M_{(\text{NO}_X)_{\text{time period}}} = \frac{\sum_{h=1}^p M(\text{NO}_X)_h}{2000} \quad (\text{Eq. F-27})$$

Where:

$M(\text{NO}_X)_{\text{time period}}$  =  $\text{NO}_X$  mass emissions in tons for the given time period (quarter, cumulative ozone season, cumulative year-to-date).

$M(\text{NO}_X)_h$  =  $\text{NO}_X$  mass emissions in lb for the hour.

## Attachment: Mercury Monitoring Provisions

p = The number of hours in the given time period (quarter, cumulative ozone season, cumulative year-to-date).

(b) When hourly NO<sub>x</sub> mass emission rate is reported in lb/hr, use Eq. F-27a.

$$M_{\{NO_x\}_{averaged}} = \frac{\sum_{h=1}^p E_{(NO_x)_h} t_h}{2000} \quad (\text{Eq. F-27 a})$$

Where:

M(NO<sub>x</sub>)time period= NO<sub>x</sub> mass emissions in tons for the given time period (quarter, cumulative ozone season, cumulative year-to-date).

E(NO<sub>x</sub>)h= NO<sub>x</sub> mass emission rate in lb/hr for the hour.

p = The number of hours in the given time period (quarter, cumulative ozone season, cumulative year-to-date).

t<sub>h</sub>= Monitoring location operating time for hour h, in hours or fraction of an hour (in equal increments that can range from one hundredth to one quarter of an hour, at the option of the permittee).

### 9. Procedures for Hg Mass Emissions.

9.1 Use the procedures in this section to calculate the hourly Hg mass emissions (in ounces) at each monitored location, for the affected unit or group of units that discharge through a common stack.

9.1.1 To determine the hourly Hg mass emissions when using a Hg concentration monitoring system that measures on a wet basis and a flow monitor, use the following equation:

$$M_h = K C_h Q_h t_h \quad (\text{Eq. F-28})$$

Where:

M<sub>h</sub>= Hg mass emissions for the hour, rounded off to three decimal places, (ounces).

K = Units conversion constant,  $9.978 \times 10^{-10}$  oz-scm/μgm-scf

C<sub>h</sub>= Hourly Hg concentration, wet basis, adjusted for bias if the bias-test procedures in appendix A to this part show that a bias-adjustment factor is necessary, (μgm/wscm).

## Attachment: Mercury Monitoring Provisions

$Q_h$  = Hourly stack gas volumetric flow rate, adjusted for bias, where the bias-test procedures in appendix A to this part shows a bias-adjustment factor is necessary, (scfh)

$t_h$  = Unit or stack operating time, as defined in 40 CFR 72.2, (hr)

9.1.2 To determine the hourly Hg mass emissions when using a Hg concentration monitoring system that measures on a dry basis or a sorbent trap monitoring system and a flow monitor, use the following equation:

$$M_h = K C_h Q_h t_h (1 - B_{ws}) \quad (\text{Eq. F-29})$$

Where:

$M_h$  = Hg mass emissions for the hour, rounded off to three decimal places, (ounces).

$K$  = Units conversion constant,  $9.978 \times 10^{-10}$  oz-scm/ $\mu$ gm-scf

$C_h$  = Hourly Hg concentration, dry basis, adjusted for bias if the bias-test procedures in appendix A to this part show that a bias-adjustment factor is necessary, ( $\mu$ gm/dscm). For sorbent trap systems, a single value of  $C_h$  ( *i.e.* , a flow-proportional average concentration for the data collection period), is applied to each hour in the data collection period, for a particular pair of traps.

$Q_h$  = Hourly stack gas volumetric flow rate, adjusted for bias, where the bias-test procedures in appendix A to this part shows a bias-adjustment factor is necessary, (scfh)

$B_{ws}$  = Moisture fraction of the stack gas, expressed as a decimal (equal to %  $H_2O$  100)

$t_h$  = Unit or stack operating time, as defined in 40 CFR 72.2, (hr)

9.2 Use the following equation to calculate quarterly and year-to-date Hg mass emissions in ounces:

$$M_{\text{time period}} = \sum_{k=1}^n M_k \quad (\text{Eq. F-30})$$

Where:

$M_{\text{time period}}$  = Hg mass emissions for the given time period *i.e.* , quarter or year-to-date, rounded to the nearest thousandth, (ounces).

$M_h$  = Hg mass emissions for the hour, rounded to three decimal places, (ounces).

$n$  = The number of hours in the given time period (quarter or year-to-date).

## Attachment: Mercury Monitoring Provisions

9.3 If heat input rate monitoring is required, follow the applicable procedures for heat input apportionment and summation in sections 5.3, 5.6 and 5.7 of this appendix.

### 10. Moisture Determination From Wet and Dry O<sub>2</sub> Readings

If a correction for the stack gas moisture content is required in any of the emissions or heat input calculations described in this appendix, and if the hourly moisture content is determined from wet- and dry-basis O<sub>2</sub> readings, use Equation F-31 to calculate the percent moisture, unless a "K" factor or other mathematical algorithm is developed as described in section 6.5.7(a) of appendix A to this part:

$$\%H_2O = \frac{(O_{2d} - O_{2w})}{O_{2d}} \times 100 \quad (\text{Eq. F-31})$$

Where:

% H<sub>2</sub>O = Hourly average stack gas moisture content, percent H<sub>2</sub>O

O<sub>2d</sub> = Dry-basis hourly average oxygen concentration, percent O<sub>2</sub>

O<sub>2w</sub> = Wet-basis hourly average oxygen concentration, percent O<sub>2</sub>

## Attachment: Mercury Monitoring Provisions

### Appendix G to Attachment—Determination of CO<sub>2</sub> Emissions

#### 1. Applicability

The procedures in this appendix may be used to estimate CO<sub>2</sub> mass emissions discharged to the atmosphere (in tons/day) as the sum of CO<sub>2</sub> emissions from combustion and, if applicable, CO<sub>2</sub> emissions from sorbent used in a wet flue gas desulfurization control system, fluidized bed boiler, or other emission controls.

#### 2. Procedures for Estimating CO<sub>2</sub> Emissions From Combustion

Use the following procedures to estimate daily CO<sub>2</sub> mass emissions from the combustion of fossil fuels. When the CFB boilers combust any nonfossil fuels (e.g., bark, wood, residue, or refuse), either use a CO<sub>2</sub> continuous emission monitoring system or apply to the DEQ for approval of a unit-specific method for determining CO<sub>2</sub> emissions.

2.1 Use the following equation to calculate daily CO<sub>2</sub> mass emissions (in tons/day) from the combustion of fossil fuels.

$$W_{CO_2} = \frac{(MW_C + MW_O) \times W_C}{2,000 MW_C} \text{ (Eq. G-1)}$$

Where:

$W_{CO_2}$  = CO<sub>2</sub> emitted from combustion, tons/day.

$MW_C$  = Molecular weight of carbon (12.0).

$MW_{O_2}$  = Molecular weight of oxygen (32.0)

$W_C$  = Carbon burned, lb/day, determined using fuel sampling and analysis and fuel feed rates.

2.1.1 Collect at least one fuel sample during each week that the unit combusts coal. Collect coal samples from a location in the fuel handling system that provides a sample representative of the fuel bunkered or consumed during the week.

2.1.2 Determine the carbon content of each fuel sample using one of the following methods: ASTM D3178–89 (Reapproved 2002) or ASTM D5373–02 (Reapproved 2007) for coal; ASTM D5291–02, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants, ultimate analysis of oil, or computations based upon ASTM D3238–95 (Reapproved 2000) and either ASTM D2502–92 (Reapproved 1996) or ASTM D2503–92 (Reapproved 1997) for oil; and computations based on ASTM D1945–96 (Reapproved 2001) or ASTM D1946–90 (Reapproved 2006) for gas (all incorporated by reference under 40 CFR 75.6).

## Attachment: Mercury Monitoring Provisions

2.1.3 Use daily fuel feed rates from company records for all fuels and the carbon content of the most recent fuel sample under this section to determine tons of carbon per day from combustion of each fuel. (All ASTM methods are incorporated by reference under 40 CFR 75.6.) Where more than one fuel is combusted during a calendar day, calculate total tons of carbon for the day from all fuels.

2.2 For an affected coal-fired unit, the estimate of daily CO<sub>2</sub> mass emissions given by equation G-1 may be adjusted to account for carbon retained in the ash using the procedures in either section 2.2.1 through 2.2.3 or section 2.2.4 of this appendix.

2.2.1 Determine the ash content of the weekly sample of coal using ASTM D3174-00, "Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal" (incorporated by reference under 40 CFR 75.6).

2.2.2 Sample and analyze the carbon content of the fly-ash according to ASTM D5373-02 (Reapproved 2007), Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke" (incorporated by reference under 40 CFR 75.6).

2.2.3 Discount the estimate of daily CO<sub>2</sub> mass emissions from the combustion of coal given by equation G-1 by the percent carbon retained in the ash using the following equation:

$$W_{\text{NCO}_2} = W_{\text{CO}_2} - \left( \frac{MW_{\text{CO}_2}}{MW_c} \right) \left( \frac{A\%}{100} \right) \left( \frac{C\%}{100} \right) W_{\text{COAL}}$$

(Eq. G-2)

where,

$W_{\text{NCO}_2}$  = Net CO<sub>2</sub> mass emissions discharged to the atmosphere, tons/day.

$W_{\text{CO}_2}$  = Daily CO<sub>2</sub> mass emissions calculated by equation G-1, tons/day.

$MW_{\text{CO}_2}$  = Molecular weight of carbon dioxide (44.0).

$MW_c$  = Molecular weight of carbon (12.0).

A% = Ash content of the coal sample, percent by weight.

C% = Carbon content of ash, percent by weight.

$W_{\text{COAL}}$  = Feed rate of coal from company records, tons/day.

2.2.4 The daily CO<sub>2</sub> mass emissions from combusting coal may be adjusted to account for carbon retained in the ash using the following equation:



## Attachment: Mercury Monitoring Provisions

$$W_{\text{NCO}_2} = .99 W_{\text{CO}_2}$$

(Eq. G-3)

where,

$W_{\text{NCO}_2}$  = Net  $\text{CO}_2$  mass emissions from the combustion of coal discharged to the atmosphere, tons/day.

.99 = Average fraction of coal converted into  $\text{CO}_2$  upon combustion.

$W_{\text{CO}_2}$  = Daily  $\text{CO}_2$  mass emissions from the combustion of coal calculated by equation G-1, tons/day.

### 3. Procedures for Estimating $\text{CO}_2$ Emissions From Sorbent

The permittee shall use either a  $\text{CO}_2$  continuous emission monitoring system or an  $\text{O}_2$  monitor and a flow monitor, or use the procedures, methods, and equations in sections 3.1 through 3.2 of this appendix to determine daily  $\text{CO}_2$  mass emissions from the sorbent (in tons).

3.1 When limestone is the sorbent material, use the equations and procedures in either section 3.1.1 or 3.1.2 of this appendix.

3.1.1 Use the following equation to estimate daily  $\text{CO}_2$  mass emissions from sorbent (in tons).

$$SE_{\text{CO}_2} = W_{\text{CaCO}_3} F_u \frac{MW_{\text{CO}_2}}{MW_{\text{CaCO}_3}}$$

(Eq. G-5)

where,

$SE_{\text{CO}_2}$  =  $\text{CO}_2$  emitted from sorbent, tons/day.

$W_{\text{CaCO}_3}$  =  $\text{CaCO}_3$  used, tons/day.

$F_u$  = 1.00, the calcium to sulfur stoichiometric ratio.

$MW_{\text{CO}_2}$  = Molecular weight of carbon dioxide (44).

$MW_{\text{CaCO}_3}$  = Molecular weight of calcium carbonate (100).

3.1.2 In lieu of using Equation G-5, any permittee who operates and maintains a certified  $\text{SO}_2$ -diluent continuous emission monitoring system (consisting of an  $\text{SO}_2$